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CERTAIN SUMMATIONS DUE TO RAMANUJAN, AND THEIR GENERALISATIONS

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Introduction

Recently, Sandham[1] has studied simple proofs of three summations due to Ramanujan (**2**, pp. 326, xxvi), namely,

$$\sum_{n=1}^{\infty} \frac{n}{e^{2n\pi}-1} = \frac{1}{24} - \frac{1}{8\pi}, \quad \sum_{n=1}^{\infty} \frac{n^{13}}{e^{2n\pi}-1} = \frac{1}{24}, \quad \sum_{n=1}^{\infty} \frac{\coth n\pi}{n^7} = \frac{19\pi^7}{56700},$$

of which the first has been established by Ramanujan himself (**2**, p. 34) in his paper on "Modular Equations and Approximations to π". Sandham has also indicated a generalisation of the above in the summation of the series

$$\sum_{n=1}^{\infty} \frac{n^{4p+1}}{e^{2n\pi}-1}, \quad \sum_{n=1}^{\infty} \frac{\coth n\pi}{n^{4p-1}} \qquad (p = 1, 2, 3, \ldots).$$

Proofs similar to those of Sandham can be given of two other summations due to Ramanujan (**2**, pp. xxvi, 352), namely,

$$\sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^5} \operatorname{sech} \frac{(2n+1)\pi}{2} = \frac{\pi^5}{768}, \quad \sum_{n=1}^{\infty} \frac{1}{n^3}\left(\coth n\pi x + x^2 \coth \frac{n\pi}{x}\right) = \frac{\pi^3}{90x}(x^4 + 5x^2 + 1),$$

of which the latter has been established by Preece[3] by the method of residues. All these summations and several other allied ones have been systematically dealt with in this paper, and are pointed out as particular cases of much more general results proved here.

Throughout this paper, a, b, α, β denote positive numbers. Writing, as usual,

$$\eta(s) = \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^s} \qquad (s > 0), \qquad \zeta(s) = \sum_{n=1}^{\infty} \frac{1}{n^s} \qquad (s > 1), \quad \zeta(0) = -\tfrac{1}{2},$$

we make use of the well-known formulæ

$$\eta(2p+1)=\frac{E_{2p}}{2(2p)!}\left(\frac{\pi}{2}\right)^{2p+1},\quad \zeta(2p)=\frac{B_{2p}}{2(2p)!}(2\pi)^{2p}\ (p=0,1,2,\ldots.),$$

where $E_0=1$, $E_2=1$, $E_4=5,\ldots.$ are Euler's numbers and $B_0=-1$, $B_2=\frac{1}{6}$, $B_4=\frac{1}{30},\cdots$ are Bernoulli's numbers.

§1. We establish the result:

$$\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)^{2q+1}}\left[a^{2q}\operatorname{sech}\frac{(2n+1)\pi b}{2a}+(-1)^q b^{2q}\operatorname{sech}\frac{(2n+1)\pi a}{2b}\right] \quad (1\cdot1)$$

$$=\frac{4}{\pi}\sum_{k=0}^{q}(-1)^k\eta(2k+1)\,\eta(2q-2k+1)\,a^{2q-2k}b^{2k},\ (q=0,1,2,3,\ldots.).$$

Using the known expansion

$$\operatorname{sech}\frac{\pi x}{2}=\frac{4}{\pi}\sum_{n=0}^{\infty}(-1)^n\frac{2n+1}{(2n+1)^2+x^2},$$

we have

$$\sum_{m=0}^{\infty}\frac{(-1)^m}{(2m+1)^{2q+1}}\operatorname{sech}\frac{(2m+1)\pi b}{2a}=\frac{4a^2}{\pi}\sum_{m=0}^{\infty}\sum_{l=0}^{\infty}\frac{(-1)^{l+m}}{(2m+1)^{2q+1}}\cdot\frac{2l+1}{(2l+1)^2a^2+(2m+1)^2b^2},$$

$$\sum_{l=0}^{\infty}\frac{(-1)^l}{(2l+1)^{2q+1}}\operatorname{sech}\frac{(2l+1)\pi a}{2b}=\frac{4b^2}{\pi}\sum_{l=0}^{\infty}\sum_{m=0}^{\infty}\frac{(-1)^{l+m}}{(2l+1)^{2q+1}}\cdot\frac{2m+1}{(2l+1)^2a^2+(2m+1)^2b^2}.$$

On multiplying these two equations respectively by a^{2q}, $(-1)^q b^{2q}$ and adding, we have

$$\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)^{2q+1}}\left[a^{2q}\operatorname{sech}\frac{(2n+1)\pi b}{2a}+(-1)^q b^{2q}\operatorname{sech}\frac{(2n+1)\pi a}{2b}\right]$$

$$=\frac{4}{\pi}\sum_{l,m=0}^{\infty}\frac{(-1)^{l+m}}{(2l+1)^{2q+1}(2m+1)^{2q+1}}\cdot\frac{(2l+1)^{2q+2}a^{2q+2}+(-1)^q(2m+1)^{2q+2}b^{2q+2}}{(2l+1)^2a^2+(2m+1)^2b^2}$$

$$=\frac{4}{\pi}\sum_{l,m=0}^{\infty}(-1)^{l+m}\sum_{k=0}^{q}(-1)^k\frac{a^{2q-2k}b^{2k}}{(2l+1)^{2k+1}(2m+1)^{2q-2k+1}}.$$

This establishes (1·1).

In particular, we note the case $q=0$ of (1·1) in the form

$$\sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} [\operatorname{sech}(2n+1)\alpha + \operatorname{sech}(2n+1)\beta] = \frac{\pi}{4}, \quad \left(\alpha\beta = \frac{\pi^2}{4}\right) \quad (1.1\,a)$$

As an immediate corollary to (1·1), we have

$$\sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^{4p+1}} \operatorname{sech} \frac{(2n+1)\pi}{2} = \frac{2}{\pi} \sum_{k=0}^{2p} (-1)^k \eta(2k+1)\,\eta(4p-2k+1),$$
$$(p=0, 1, 2, \ldots.) \quad (1.1\,b)$$

of which the case $p=1$ furnishes Ramanujan's result.

The result complementary to (1·1) which examines it for *negative* integral values of q is given by

$$\alpha^q \sum_{n=0}^{\infty} (-1)^n \frac{(2n+1)^{2q-1}}{\cosh(2n+1)\alpha} + (-1)^q \beta^q \sum_{n=0}^{\infty} (-1)^n \frac{(2n+1)^{2q-1}}{\cosh(2n+1)\beta} = 0,$$
$$\left(\alpha\beta = \frac{\pi^2}{4};\ q=1, 2, 3, \ldots.\right) \quad (1\cdot2).$$

To prove this, we consider

$$2\sum_{n=0}^{\infty} (-1)^n e^{-\frac{(2n+1)\pi x}{2}} = \operatorname{sech} \frac{\pi x}{2} = \frac{2}{\pi i} \sum_{n=0}^{\infty} (-1)^n \left[\frac{1}{x - i(2n+1)} - \frac{1}{x + i(2n+1)}\right], \quad (x>0).$$

Term-wise differentiation $(2q-1)$ times w.r.t x. yields

$$2\sum_{n=0}^{\infty} (-1)^n (2n+1)^{2q-1} e^{-\frac{(2n+1)\pi x}{2}} = \left(\frac{2}{\pi}\right)^{2q} \frac{(2q-1)!}{i} \sum_{n=0}^{\infty} (-1)^n \times$$
$$\times \left[\frac{1}{\{x - i(2n+1)\}^{2q}} - \frac{1}{\{x + i(2n+1)\}^{2q}}\right], \quad (x>0).$$

Making these substitutions, we have, for $x>0$,

$$\sum_{n=0}^{\infty} (-1)^n (2n+1)^{2q-1} \operatorname{sech} \frac{(2n+1)\pi x}{2}$$
$$= 2\sum_{n=0}^{\infty} (-1)^n (2n+1)^{2q-1} \sum_{m=0}^{\infty} (-1)^m e^{-\frac{(2m+1)(2n+1)\pi x}{2}}$$
$$= 2\sum_{m=0}^{\infty} (-1)^m \sum_{n=0}^{\infty} (-1)^n (2n+1)^{2q-1} e^{-\frac{(2n+1)(2m+1)\pi x}{2}}$$
$$= \left(\frac{2}{\pi}\right)^{2q} \frac{(2q-1)!}{i} \sum_{m=0}^{\infty} (-1)^m \sum_{n=0}^{\infty} (-1)^n \left[\frac{1}{\{(2m+1)x - i(2n+1)\}^{2q}} - \frac{1}{\{(2m+1)x + i(2n+1)\}^{2q}}\right]$$

This gives

$$\sum_{m=0}^{\infty}(-1)^m(2m+1)^{2q-1}\operatorname{sech}\frac{(2m+1)\pi a}{2b}$$

$$=\left(\frac{2b}{\pi}\right)^{2q}\frac{(2q-1)!}{i}\sum_{l,\,m=0}^{\infty}(-1)^{l+m}\left[\frac{1}{\{(2l+1)a-i(2m+1)b\}^{2q}}\right.$$

$$\left.-\frac{1}{\{(2l+1)a+i(2m+1)b\}^{2q}}\right],$$

$$\sum_{l=0}^{\infty}(-1)^l(2l+1)^{2q-1}\operatorname{sech}\frac{(2l+1)\pi b}{2a}=(-1)^q\left(\frac{2a}{\pi}\right)^{2q}\frac{(2q-1)!}{i}\sum_{l,\,m=0}^{\infty}(-1)^{l+m}\cdot$$

$$\cdot\left[\frac{1}{\{(2l+1)a+i(2m+1)b\}^{2q}}-\frac{1}{\{(2l+1)a-i(2m+1)b\}^{2q}}\right].$$

Hence

$$\sum_{n=0}^{\infty}(-1)^n(2n+1)^{2q-1}\left[a^{2q}\operatorname{sech}\frac{(2n+1)\pi a}{2b}+(-1)^q b^{2q}\operatorname{sech}\frac{(2n+1)\pi b}{2a}\right]$$

$$=0,$$

which establishes (1·2).

In particular, we note the case $q=1$ of (1.2):

$$\alpha\sum_{n=0}^{\infty}(-1)^n\frac{2n+1}{\cosh(2n+1)\alpha}=\beta\sum_{n=0}^{\infty}(-1)^n\frac{2n+1}{\cosh(2n+1)\beta},\quad\left(\alpha\beta=\frac{\pi^2}{4}\right).\tag{1.2a}$$

As an immediate corollary to (1·2), we recover a result of Ramanujan (**2**, p. 326):

$$\sum_{n=0}^{\infty}(-1)^n(2n+1)^{4p-1}\operatorname{sech}\frac{(2n+1)\pi}{2}=0,\quad(p=1,2,3,\ldots).\tag{1.2b}$$

§ 2. We here establish the result:

$$\sum_{n=1}^{\infty}\frac{1}{n^{2q-1}}\left[a^{2q-2}\coth\frac{n\pi b}{a}+(-1)^q b^{2q-2}\coth\frac{n\pi a}{b}\right]$$

$$=\begin{cases}\dfrac{\pi}{6}\left(\dfrac{a}{b}-\dfrac{b}{a}\right)-(\log a-\log b) & \text{for } q=1,\\[2ex] \dfrac{2}{\pi ab}\displaystyle\sum_{k=0}^{q}(-1)^{k-1}\zeta(2k)\,\zeta(2q-2k)\,a^{2q-2k}\,b^{2k} & \text{for } q=2,3,4,\ldots,\end{cases}\tag{2.1}$$

of which the case $q=2$ furnishes Ramanujan's result.

We first discuss the case $q>1$. Using the expansion

$$\coth\pi x-\frac{1}{\pi x}=\frac{2x}{\pi}\sum_{n=1}^{\infty}\frac{1}{n^2+x^2},$$

we have

$$\sum_{m=1}^{\infty} \frac{1}{m^{2q-1}} \coth \frac{m\pi b}{a} - \frac{a}{\pi b} \sum_{m=1}^{\infty} \frac{1}{m^{2q}} = \frac{2ab}{\pi} \sum_{m=1}^{\infty} \sum_{l=1}^{\infty} \frac{1}{m^{2q-2}(l^2a^2 + m^2b^2)},$$

$$\sum_{l=1}^{\infty} \frac{1}{l^{2q-1}} \coth \frac{l\pi a}{b} - \frac{b}{\pi a} \sum_{l=1}^{\infty} \frac{1}{l^{2q}} = \frac{2ab}{\pi} \sum_{l=1}^{\infty} \sum_{m=1}^{\infty} \frac{1}{l^{2q-2}(l^2a^2 + m^2b^2)}.$$

On multiplying these two equations respectively by $a^{2q-2}, (-1)^q b^{2q-2}$ and adding, we have

$$\sum_{n=1}^{\infty} \frac{1}{n^{2q-1}} \left[a^{2q-2} \coth \frac{n\pi b}{a} + (-1)^q b^{2q-2} \coth \frac{n\pi a}{b} \right]$$

$$- \frac{1}{\pi ab} \{a^{2q} + (-1)^q b^{2q}\} \sum_{n=1}^{\infty} \frac{1}{n^{2q}}$$

$$= \frac{2ab}{\pi} \sum_{l,\, m=1}^{\infty} \frac{1}{l^{2q-2} m^{2q-2}} \frac{l^{2q-2}a^{2q-2} + (-1)^q m^{2q-2} b^{2q-2}}{l^2a^2 + m^2b^2}$$

$$= \frac{2}{\pi ab} \sum_{l,\, m=1}^{\infty} \sum_{k=1}^{q-1} (-1)^{k-1} \frac{a^{2q-2k} b^{2k}}{l^{2k} m^{2q-2k}},$$

which completes the proof of (2.1) for $q > 1$.

In the case $q = 1$, we transform the result to be proved into the equivalent form

$$\sum_{n=1}^{\infty} \frac{1}{n} \left(\frac{1}{e^{2n\beta} - 1} - \frac{1}{e^{2n\alpha} - 1} \right) = \frac{1}{12} (\alpha - \beta) - \frac{1}{4} (\log \alpha - \log \beta), \ (\alpha\beta = \pi^2), \quad (2{\cdot}1\,a)$$

by substituting from

$$\coth n\pi x = 1 + \frac{2}{e^{2n\pi x} - 1}.$$

Now (2.1 *a*) is substantially equivalent to the following result due to Ramanujan (**2**, p. 32):

$$\alpha^{\frac{1}{4}} e^{-\frac{1}{12}\alpha} \prod_{n=1}^{\infty} (1 - e^{-2n\alpha}) = \beta^{\frac{1}{4}} e^{-\frac{1}{12}\beta} \prod_{n=1}^{\infty} (1 - e^{-2n\beta}), \qquad (\alpha\beta = \pi^2) \qquad (2{\cdot}1)$$

Thus our result follows at once on taking logarithms in (2·1) and observing that, for $x > 0$,

$$\sum_{n=1}^{\infty} \frac{1}{n(e^{2nx} - 1)} = \sum_{n=1}^{\infty} \frac{1}{n} \sum_{m=1}^{\infty} e^{-2mnx} = \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{1}{n} e^{-2mnx} = -\sum_{m=1}^{\infty} \log (1 - e^{-2mx}).$$

As an immediate corollary to (2.1), we have

$$\sum_{n=1}^{\infty} \frac{1}{n^{4p-1}} \coth n\pi = \frac{1}{\pi} \sum_{k=0}^{2p} (-1)^{k-1} \zeta(2k)\, \zeta(4p - 2k), \ (p = 1, 2, 3, \ldots.) \qquad (2{\cdot}1\,b)$$

of which the case $p = 2$ furnishes Ramanujan's result.

Also the limiting form of our result

$$\sum_{n=1}^{\infty} \frac{1}{n}\left(\coth \frac{n\pi b}{a} - \coth \frac{n\pi a}{b}\right) = \frac{\pi}{6}\left(\frac{a}{b} - \frac{b}{a}\right) - (\log a - \log b),$$

when a and b tend to equality, reads:

$$\sum_{n=1}^{\infty} \frac{1}{\sinh^2 n\pi} = \frac{1}{6} - \frac{1}{2\pi}. \tag{2.1 c}$$

The companion result to (2.1) which examines it for integral values of $q \leqq 0$ is given by

$$\alpha^q \left(\frac{B_{2q}}{4q} + (-1)^q \sum_{n=1}^{\infty} \frac{n^{2q-1}}{e^{2n\alpha} - 1}\right) + (-1)^{q-1} \beta^q \left(\frac{B_{2q}}{4q} + (-1)^q \sum_{n=1}^{\infty} \frac{n^{2q-1}}{e^{2n\beta} - 1}\right) \tag{2·2}$$

$$= \begin{cases} \frac{1}{4} & \text{for } q = 1, \\ 0 & \text{for } q = 2, 3, 4, \ldots\ldots, \end{cases} \qquad (\alpha\beta = \pi^2).$$

We first discuss the case $q > 1$. Consider

$$\sum_{n=1}^{\infty} e^{-2n\pi x} = \frac{1}{e^{2\pi x} - 1} = -\frac{1}{2} + \frac{1}{2\pi}\left[\frac{1}{x} + \sum_{n=1}^{\infty} \left\{\frac{1}{x + in} + \frac{1}{x - in}\right\}\right], (x > 0).$$

Termwise differentiation $(2q - 1)$ times w. r. t. x yields

$$\sum_{n=1}^{\infty} n^{2q-1} e^{-2n\pi x} = \frac{(2q-1)!}{(2\pi)^{2q}}\left[\frac{1}{x^{2q}} + \sum_{n=1}^{\infty} \left\{\frac{1}{(x + in)^{2q}} + \frac{1}{(x - in)^{2q}}\right\}\right], (x > 0).$$

With these substitutions, we have, for $x > 0$,

$$\sum_{n=1}^{\infty} \frac{n^{2q-1}}{e^{2n\pi x} - 1} = \sum_{n=1}^{\infty} n^{2q-1} \sum_{m=1}^{\infty} e^{-2mn\pi x} = \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} n^{2q-1} e^{-2mn\pi x}$$

$$= \frac{(2q-1)!}{(2\pi)^{2q}}\left[\frac{\zeta(2q)}{x^{2q}} + \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \left\{\frac{1}{(mx + in)^{2q}} + \frac{1}{(mx - in)^{2q}}\right\}\right].$$

This gives, on substituting for $\zeta(2q)$,

$$\sum_{m=1}^{\infty} \frac{m^{2q-1}}{e^{\frac{2m\pi a}{b}} - 1} = \frac{B_{2q}}{4q}\left(\frac{b}{a}\right)^{2q} + \left(\frac{b}{2\pi}\right)^{2q} (2q-1)! \sum_{l,\, m=1}^{\infty} \left\{\frac{1}{(la + imb)^{2q}} + \frac{1}{(la - imb)^{2q}}\right\},$$

$$\sum_{l=1}^{\infty} \frac{l^{2q-1}}{e^{\frac{2l\pi b}{a}} - 1} = \frac{B_{2q}}{4q}\left(\frac{a}{b}\right)^{2q} + \left(\frac{a}{2\pi}\right)^{2q} (-1)^q (2q-1)! \sum_{l,\, m=1}^{\infty} \left\{\frac{1}{(la - imb)^{2q}} + \frac{1}{(la + imb)^{2q}}\right\}$$

Hence we have

$$\sum_{n=1}^{\infty} n^{2q-1}\left[\frac{a^{2q}}{e^{\frac{2n\pi a}{b}}-1}+(-1)^{q-1}\frac{b^{2q}}{e^{\frac{2n\pi b}{a}}-1}\right]=\frac{B_{2q}}{4q}\{b^{2q}\mp(-1)^{q-1}a^{2q}\},$$

which is easily seen to be equivalent to (2.2) for $q>1$.

The case $q=1$ is due to Ramanujan [2, p. 32]:

$$\alpha\left(\frac{1}{24}-\sum_{n=1}^{\infty}\frac{n}{e^{2n\alpha}-1}\right)+\beta\left(\frac{1}{24}-\sum_{n=1}^{\infty}\frac{n}{e^{2n\beta}-1}\right)=\tfrac{1}{4}, \qquad (\alpha\beta=\pi^2),$$

and follows at once by taking logarithmic derivatives in (2·1).

s an immediate corollary to (2.2), we have

$$\sum_{n=1}^{\infty}\frac{n^{4p+1}}{e^{2n\pi}-1}=\begin{cases}\dfrac{1}{24}-\dfrac{1}{8\pi} & \text{for } p=0,\\[2ex] \dfrac{B_{4p+2}}{8p+4} & \text{for } p=1,2,3,\ldots\ldots.\end{cases} \qquad (2.2\,b)$$

Also the limiting form of our result

$$\sum_{n=1}^{\infty} n^{4p-1}\left[\frac{\left(\frac{a}{b}\right)^{2p}}{e^{2n\pi\left(\frac{a}{b}\right)}-1}-\frac{\left(\frac{b}{a}\right)^{2p}}{e^{2n\pi\left(\frac{b}{a}\right)}-1}\right]=\frac{B_{4p}}{8p}\left[\left(\frac{b}{a}\right)^{2p}-\left(\frac{a}{b}\right)^{2p}\right], \qquad (p=1,2,3,\ldots.),$$

when a and b tend to equality, furnishes another result of Ramanujan (2, p. xxvi):

$$\pi\sum_{n=1}^{\infty}\frac{n^{4p}}{\sinh^2 n\pi}-4p\sum_{n=1}^{\infty}\frac{n^{4p-1}}{e^{2n\pi}-1}=\tfrac{1}{2}B_{4p}, \quad (p=1,\ 2,\ 3,\ldots.). \qquad (2.2\,c)$$

§ 3. We here establish the result:

$$\sum_{n=1}^{\infty}\frac{(-1)^{n-1}}{n^{2q-1}}\left[a^{2q-2}\operatorname{cosech}\frac{n\pi b}{a}+(-1)^q b^{2q-2}\operatorname{cosech}\frac{n\pi a}{b}\right] \qquad (3.1)$$

$$=\frac{2}{\pi ab}\sum_{k=0}^{q}(-1)^k\left(1-\frac{2}{2^{2k}}\right)\zeta(2k)\left(1-\frac{2}{2^{2q-2k}}\right)\zeta(2q-2k)\,a^{2q-2k}b^{2k}, \qquad (q=1,2,3,\ldots.)$$

We first discuss the case $q>1$. Using the expansion

$$\operatorname{cosech}\pi x-\frac{1}{\pi x}=-\frac{2x}{\pi}\sum_{n=1}^{\infty}\frac{(-1)^{n-1}}{n^2+x^2},$$

we have

$$\sum_{m=1}^{\infty} \frac{(-1)^{m-1}}{m^{2q-1}} \operatorname{cosech} \frac{m\pi b}{a} - \frac{a}{\pi b} \sum_{m=1}^{\infty} \frac{(-1)^{m-1}}{m^{2q}}$$

$$= -\frac{2ab}{\pi} \sum_{m=1}^{\infty} \sum_{l=1}^{\infty} \frac{(-1)^{(l-1)+(m-1)}}{m^{2q-2}} \frac{1}{l^2a^2 + m^2b^2},$$

$$\sum_{l=1}^{\infty} \frac{(-1)^{l-1}}{l^{2q-1}} \operatorname{cosech} \frac{l\pi a}{b} - \frac{b}{\pi a} \sum_{l=1}^{\infty} \frac{(-1)^{l-1}}{l^{2q}}$$

$$= -\frac{2ab}{\pi} \sum_{l=1}^{\infty} \sum_{m=1}^{\infty} \frac{(-1)^{(l-1)+(m-1)}}{l^{2q-2}} \frac{1}{l^2a^2 + m^2b^2}.$$

On multiplying these two equations respectively by a^{2q-2}, $(-1)^q b^{2q-2}$ and adding, we have

$$\sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n^{2q-1}} \left[a^{2q-2} \operatorname{cosech} \frac{n\pi b}{a} + (-1)^q b^{2q-2} \operatorname{cosech} \frac{n\pi a}{b} \right]$$

$$- \frac{1}{\pi ab} \{a^{2q} + (-1)^q b^{2q}\} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n^{2q}}$$

$$= -\frac{2ab}{\pi} \sum_{l,m=1}^{\infty} \frac{(-1)^{(l-1)+(m-1)}}{l^{2q-2} m^{2q-2}} \frac{l^{2q-2}a^{2q-2} + (-1)^q m^{2q-2} b^{2q-2}}{l^2a^2 + m^2b^2}$$

$$= -\frac{2}{\pi ab} \sum_{l,m=1}^{\infty} (-1)^{(l-1)+(m-1)} \sum_{k=1}^{q-1} (-1)^{k-1} \frac{a^{2q-2k} b^{2k}}{l^{2k} m^{2q-2k}},$$

which yields (3.1) for $q > 1$, on substituting from

$$\sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n^s} = \left(1 - \frac{2}{2^s}\right) \zeta(s), \qquad (s > 1).$$

When $q = 1$, the result to be proved is the same as

$$\sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n} (\operatorname{cosech} n\beta - \operatorname{cosech} n\alpha) = \frac{1}{12} (\alpha - \beta), \qquad (\alpha\beta = \pi^2). \quad (3.1\,a)$$

But this is substantially equivalent to the following result of Ramanujan (**2**, p. 23):

$$e^{\frac{1}{24}\alpha} \prod_{n=1}^{\infty} (1 + e^{-(2n-1)\alpha}) = e^{\frac{1}{24}\beta} \prod_{n=1}^{\infty} (1 + e^{-(2n-1)\beta}), \qquad (\alpha\beta = \pi^2). \quad (3.1)$$

Thus, our result follows at once on taking logarithms in (3.1) and observing that, for $x > 0$,

$$\sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n \sinh nx} = 2 \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n} \sum_{m=1}^{\infty} e^{-(2m-1)nx} = 2 \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{(-)^{n-1}}{n} e^{-n(2m-1)x}$$

$$= 2 \sum_{m=1}^{\infty} \log (1 + e^{-(2m-1)x})$$

As an immediate corollary to (3.1), we have

$$\sum_{n=1}^{\infty}\frac{(-1)^{n-1}}{n^{4p-1}}\operatorname{cosech} n\pi=\frac{1}{\pi}\sum_{k=0}^{2p}(-1)^k\left(1-\frac{2}{2^{2k}}\right)\zeta(2k)\left(1-\frac{2}{2^{4p-2k}}\right)\cdot$$
$$\cdot\zeta(4p-2k),\quad (p=1,2,3,\ldots.). \qquad (3.1\,b)$$

Also the limiting form of our result

$$\sum_{n=1}^{\infty}\frac{(-1)^{n-1}}{n}\left(\operatorname{cosech}\frac{n\pi b}{a}-\operatorname{cosech}\frac{n\pi a}{b}\right)=\frac{\pi}{12}\left(\frac{a}{b}-\frac{b}{a}\right),$$

when a and b tend to equality, reads:

$$\sum_{n=1}^{\infty}(-1)^{n-1}\frac{\cosh n\pi}{\sinh^2 n\pi}=\frac{1}{12}.$$

The companion result to (3·1) which examines it for integral values of $q\leqq 0$ is given by

$$\alpha^q\sum_{n=1}^{\infty}(-1)^{n-1}\frac{n^{2q-1}}{\sinh n\alpha}+(-1)^{q-1}\beta^q\sum_{n=1}^{\infty}(-1)^{n-1}\frac{n^{2q-1}}{\sinh n\beta} \qquad (3.2)$$
$$=\begin{cases}\frac{1}{2} & \text{for } q=1,\\ 0 & \text{for } q=2,\ 3,\ 4,\ldots.,\end{cases}\qquad (\alpha\beta=\pi^2).$$

We first discuss the case $q>1$. Consider

$$\sum_{n=1}^{\infty}(-1)^{n-1}e^{-n\pi x}=\frac{1}{e^{\pi x}+1}=\frac{1}{2}-\frac{1}{\pi}\sum_{n=1}^{\infty}\left\{\frac{1}{x+i(2n-1)}+\frac{1}{x-i(2n-1)}\right\},$$
$$(x>0).$$

Termwise differentiation $(2q-1)$ times w. r. t. x yields

$$\sum_{n=1}^{\infty}(-1)^{n-1}n^{2q-1}e^{-n\pi x}=-\frac{(2q-1)!}{\pi^{2q}}\sum_{n=1}^{\infty}\left[\frac{1}{\{x+i(2n-1)\}^{2q}}\right.$$
$$\left.+\frac{1}{\{x-i(2n-1)\}^{2q}}\right],\quad (x>0).$$

With these substitutions, we have, for $x>0$,

$$\sum_{n=1}^{\infty}(-1)^{n-1}n^{2q-1}\operatorname{cosech} n\pi x=2\sum_{n=1}^{\infty}(-1)^{n-1}n^{2q-1}\sum_{m=1}^{\infty}e^{-(2m-1)n\pi x}$$
$$=2\sum_{m=1}^{\infty}\sum_{n=1}^{\infty}(-1)^{n-1}n^{2q-1}e^{-n(2m-1)\pi x}$$
$$=-\frac{2(2q-1)!}{\pi^{2q}}\sum_{m=1}^{\infty}\sum_{n=1}^{\infty}\left[\frac{1}{\{(2m-1)x+i(2n-1)\}^{2q}}\right.$$
$$\left.+\frac{1}{\{(2m-1)x-i(2n-1)\}^{2q}}\right].$$

This gives

$$\sum_{m=1}^{\infty}(-1)^{m-1}\, m^{2q-1}\,\operatorname{cosech}\frac{m\pi a}{b}$$

$$=-2\left(\frac{b}{\pi}\right)^{2q}(2q-1)\,!\sum_{l,\,m=1}^{\infty}\sum\left[\frac{1}{\{(2l-1)\,a+i\,(2m-1)\,b\}^{2q}}\right.$$

$$\left.+\frac{1}{\{(2l-1)\,a-i\,(2m-1)\,b\}^{2q}}\right],$$

$$\sum_{l=1}^{\infty}(-1)^{l-1}\, l^{2q-1}\,\operatorname{cosech}\frac{l\pi b}{a}$$

$$=-2\left(\frac{a}{\pi}\right)^{2q}(-1)^{q}(2q-1)\,!\sum_{l,\,m=1}^{\infty}\sum\left[\frac{1}{\{(2l-1)\,a-i\,(2m-1)\,b\}^{2q}}\right.$$

$$\left.+\frac{1}{\{(2l-1)\,a+i\,(2m-1)\,b\}^{2q}}\right].$$

Hence we have

$$\sum_{n=1}^{\infty}(-1)^{n-1}\, n^{2q-1}\left[a^{2q}\operatorname{cosech}\frac{n\pi a}{b}+(-1)^{q-1}\,b^{2q}\operatorname{cosech}\frac{n\pi b}{a}\right]=0,$$

which establishes (3.2) for $q>1$.

The case $q=1$ is due to Cauchy (**4**, p. 55):

$$\alpha\sum_{n=1}^{\infty}(-1)^{n-1}\frac{n}{\sinh n\alpha}+\beta\sum_{n=1}^{\infty}(-1)^{n-1}\frac{n}{\sinh n\beta}=\tfrac{1}{2}, \qquad (\alpha\beta=\pi^2), \quad (3.2a)$$

and is established by the method of residues. But it is interesting that it follows at once by taking logarithmic derivatives in the relation (4·1) of the next section.

As an immediate corollary to (3.2), we have

$$\sum_{n=1}^{\infty}(-1)^{n-1}\frac{n^{4p+1}}{\sinh n\pi}=\begin{cases}\dfrac{1}{4\pi} & \text{for } p=0,\\ 0 & \text{for } p=1,\ 2,\ 3,\ldots.\end{cases} \qquad (3.2b)$$

§ 4. We here establish the result:

$$\sum_{n=1}^{\infty}\frac{1}{(2n-1)^{2q-1}}\left[a^{2q-2}\tanh\frac{(2n-1)\,\pi b}{2a}+(-1)^{q}b^{2q-2}\tanh\frac{(2n-1)\,\pi a}{2b}\right]$$

$$=\begin{cases}-\tfrac{1}{2}(\log a-\log b) & \text{for } q=1,\\ \dfrac{4}{\pi ab}\displaystyle\sum_{k=1}^{q-1}(-1)^{q-1}\left(1-\frac{1}{2^{2k}}\right)\zeta(2k)\cdot\left(1-\frac{1}{2^{2q-2k}}\right)\cdot & \\ \qquad\cdot\,\zeta(2q-2k)\,a^{2q-2k}b^{2k} & \text{for } q=2,3,4,\ldots.\end{cases} \qquad (4.1)$$

We first discuss the case $q > 1$. Using the expansion

$$\tanh \frac{\pi x}{2} = \frac{4x}{\pi} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2 + x^2},$$

we have

$$\sum_{m=1}^{\infty} \frac{1}{(2m-1)^{2q-1}} \tanh \frac{(2m-1)\pi b}{2a}$$

$$= \frac{4ab}{\pi} \sum_{m=1}^{\infty} \sum_{l=1}^{\infty} \frac{1}{(2m-1)^{2q-2}} \frac{1}{(2l-1)^2 a^2 + (2m-1)^2 b^2},$$

$$\sum_{l=1}^{\infty} \frac{1}{(2l-1)^{2q-1}} \tanh \frac{(2l-1)\pi a}{2b}$$

$$= \frac{4ab}{\pi} \sum_{l=1}^{\infty} \sum_{m=1}^{\infty} \frac{1}{(2l-1)^{2q-2}} \frac{1}{(2l-1)^2 a^2 + 2m-1)^2 b^2}.$$

On multiplying these two equations respectively by a^{2q-2}, $(-1)^q b^{2q-2}$ and adding, we have

$$\sum_{n=1}^{\infty} \frac{1}{(2n-1)^{2q-1}} \left[a^{2q-2} \tanh \frac{(2n-1)\pi b}{2a} + (-1)^q b^{2q-2} \tanh \frac{(2n-1)\pi a}{2b} \right]$$

$$= \frac{4ab}{\pi} \sum_{l,\, m=1}^{\infty} \frac{1}{(2l-1)^{2q-2}(2m-1)^{2q-2}} \frac{(2l-1)^{2q-2} a^{2q-2} + (-1)^q (2m-1)^{2q-2} b^{2q-2}}{(2l-1)^2 a^2 + (2m-1)^2 b^2}$$

$$= \frac{4}{\pi ab} \sum_{l,\, m=1}^{\infty} \sum_{k=1}^{q-1} (-1)^{k-1} \frac{a^{2q-2k}\, b^{2k}}{(2l-1)^{2k} (2m-1)^{2q-2k}},$$

which yields (4.1) for $q > 1$, on substituting from

$$\sum_{n=1}^{\infty} \frac{1}{(2n-1)^s} = \left(1 - \frac{1}{2^s}\right) \zeta(s) \qquad (s > 1).$$

In the case $q = 1$, we throw the result to be proved into the equivalent form

$$\sum_{n=1}^{\infty} \frac{1}{2n-1} \left(\frac{1}{e^{(2n-1)\beta} + 1} - \frac{1}{e^{(2n-1)\alpha} + 1} \right) = \tfrac{1}{8} (\log \alpha - \log \beta), \ (\alpha\beta = \pi^2), \ (4.1\, a)$$

by substituting from

$$\tanh \frac{(2n-1)\pi x}{2} = 1 - \frac{2}{e^{(2n-1)\pi x} + 1}.$$

But (4.1 *a*) is substantially equivalent to the following result:

$$\alpha^{\frac{1}{4}} \prod_{n=1}^{\infty} \left(\frac{1 + e^{-n\alpha}}{1 - e^{-n\alpha}} \right)^{(-1)^{n-1}} = \beta^{\frac{1}{4}} \prod_{n=1}^{\infty} \left(\frac{1 + e^{-n\beta}}{1 - e^{-n\beta}} \right)^{(-1)^{n-1}}, \qquad (\alpha\beta = \pi^2), \qquad (4.1)$$

which is easily deduced from (2·1) and (3·1) as follows: Thus, multiplying corresponding sides of (2·1) and (3·1), we have

$$\alpha^{\frac{1}{4}} e^{-\frac{1}{24}\alpha} \prod_{n=1}^{\infty} \left(1 + (-1)^{n-1} e^{-n\alpha}\right) = \beta^{\frac{1}{4}} e^{-\frac{1}{24}\beta} \prod_{n=1}^{\infty} \left(1 + (-1)^{n-1} e^{-n\beta}\right), \quad (\alpha\beta = \pi^2).$$

If we now divide by the corresponding sides of this relation those of (2·1), we have

$$e^{-\frac{1}{24}\alpha} \prod_{n=1}^{\infty} \left(1 - (-1)^{n-1} e^{-n\alpha}\right) = e^{-\frac{1}{24}\beta} \prod_{n=1}^{\infty} \left(1 - (-1)^{n-1} e^{-n\beta}\right), \quad (\alpha\beta = \pi^2).$$

These last two relations at once yield (4·1) on division.

Now, our result (4.1 *a*) follows at once on taking logarithms in (4·1) and observing that, for $x > 0$,

$$\sum_{n=1}^{\infty} \frac{1}{(2n-1)\left(e^{(2n-1)x} + 1\right)} = \sum_{n=1}^{\infty} \frac{1}{2n-1} \sum_{m=1}^{\infty} (-1)^{m-1} e^{-m(2n-1)x}$$

$$= \sum_{m=1}^{\infty} (-1)^{m-1} \sum_{n=1}^{\infty} \frac{1}{2n-1} e^{-(2n-1)mx} = \frac{1}{2} \sum_{m=1}^{\infty} (-1)^{m-1} \log\left(\frac{1+e^{-mx}}{1-e^{-mx}}\right).$$

As an immediate corollary to (4·1), we have

$$\sum_{n=1}^{\infty} \frac{1}{(2n-1)^{4p-1}} \tanh \frac{(2n-1)\pi}{2}$$

$$= \frac{2}{\pi} \sum_{k=1}^{2p-1} (-1)^{k-1} \left(1 - \frac{1}{2^{2k}}\right) \zeta(2k) \left(1 - \frac{1}{2^{4p-2k}}\right) \zeta(4p-2k),$$

$$(p = 1, 2, 3, \ldots). \quad (4.1\ b)$$

Also the limiting form of our result

$$\sum_{n=1}^{\infty} \frac{1}{2n-1} \left[\tanh \frac{(2n-1)\pi a}{2b} - \tanh \frac{(2n-1)\pi b}{2a}\right] = \frac{1}{2}(\log a - \log b),$$

when a and b tend to equality, reads:

$$\sum_{n=1}^{\infty} \operatorname{sech}^2 \frac{(2n-1)\pi}{2} = \frac{1}{2\pi}. \quad (4.1\ c)$$

The companion result to (4.1) which examines it for integral values of $q \leqq 0$ is given by

$$\alpha^q \left((2^{2q-1} - 1) \frac{B_{2q}}{4q} + (-1)^q \sum_{n=1}^{\infty} \frac{(2n-1)^{2q-1}}{e^{(2n-1)\alpha} + 1}\right)$$

$$+ (-1)^{q-1} \beta^q \left((2^{2q-1} - 1) \frac{B_{2q}}{4q} + (-1)^q \sum_{n=1}^{\infty} \frac{(2n-1)^{2q-1}}{e^{(2n-1)\beta} + 1}\right) = 0,$$

$$(\alpha\beta = \pi^2;\ q = 1, 2, 3, \ldots). \quad (4{\cdot}2)$$

We first discuss the case $q > 1$. Consider

$$\sum_{n=1}^{\infty} e^{-(2n-1)\pi x} = \tfrac{1}{2}\operatorname{cosech} \pi x = \frac{1}{2\pi}\left[\frac{1}{x} - \sum_{n=1}^{\infty}(-1)^{n-1}\left\{\frac{1}{x+in} + \frac{1}{x-in}\right\}\right], \qquad (x > 0).$$

Term wise differentiation $(2q-1)$ ltimes w.r.t. x yields

$$\sum_{n=1}^{\infty}(2n-1)^{2q-1} e^{-(2n-1)\pi x} = \frac{(2q-1)!}{2\pi^{2q}}\left[\frac{1}{x^{2q}} - \sum_{n=1}^{\infty}(-1)^{n-1}\left\{\frac{1}{(x+in)^{2q}} + \frac{1}{(x-in)^{2q}}\right\}\right], \qquad (x > 0).$$

With these substitutions, we have, for $x > 0$,

$$\sum_{n=1}^{\infty}\frac{(2n-1)^{2q-1}}{e^{(2n-1)\pi x}+1} = \sum_{n=1}^{\infty}(2n-1)^{2q-1}\sum_{m=1}^{\infty}(-1)^{m-1}e^{-m(2n-1)\pi x}$$

$$= \sum_{m=1}^{\infty}(-1)^{m-1}\sum_{n=1}^{\infty}(2n-1)^{2q-1}\, e^{-(2n-1)m\pi x}$$

$$= \frac{(2q-1)!}{2\pi^{2q}}\left[\left(1 - \frac{1}{2^{2q-1}}\right)\frac{\zeta(2q)}{x^{2q}}\right.$$

$$\left. - \sum_{m=1}^{\infty}\sum_{n=1}^{\infty}(-1)^{(m-1)+(n-1)}\left\{\frac{1}{(mx+in)^{2q}} + \frac{1}{(mx-in)^{2q}}\right\}\right].$$

This gives, on substituting for $\zeta(2q)$,

$$\sum_{m=1}^{\infty}\frac{(2m-1)^{2q-1}}{e^{\frac{(2m-1)\pi a}{b}}+1} = (2^{2q-1}-1)\frac{B_{2q}}{4q}\cdot\left(\frac{b}{a}\right)^{2q} - \tfrac{1}{2}\left(\frac{b}{\pi}\right)^{2q}(2q-1)!\times$$

$$\times \sum_{l,m=1}^{\infty}(-1)^{(l-1)+(m-1)}\left\{\frac{1}{(la+imb)^{2q}} + \frac{1}{(la-imb)^{2q}}\right\},$$

$$\sum_{l=1}^{\infty}\frac{(2l-1)^{2q-1}}{e^{\frac{(2l-1)\pi b}{a}}+1} = (2^{2q-1}-1)\frac{B_{2q}}{4q}\cdot\left(\frac{a}{b}\right)^{2q} - \tfrac{1}{2}\left(\frac{a}{\pi}\right)^{2q}(-1)^{q}(2q-1)!\times$$

$$\times \sum_{l,m=1}^{\infty}(-1)^{(l-1)+(m-1)}\left\{\frac{1}{(la-imb)^{2q}} + \frac{1}{(la+imb)^{2q}}\right\}.$$

Hence we have

$$\sum_{n=1}^{\infty}(2n-1)^{2q-1}\left[\frac{a^{2q}}{e^{\frac{(2n-1)\pi a}{b}}+1} + (-1)^{q-1}\frac{b^{2q}}{e^{\frac{(2n-1)\pi b}{a}}+1}\right]$$

$$= (2^{2q-1}-1)\frac{B_{2q}}{4q}\{b^{2q} + (-1)^{q-1}a^{2q}\},$$

which is easily seen to be equivalent to (4.2) for $q > 1$.

The case $q = 1$ results immediately on taking logarithmic derivatives in the relation (3.1) of the previous section:

$$\alpha\left(\frac{1}{24} - \sum_{n=1}^{\infty} \frac{2n-1}{e^{(2n-1)\alpha}+1}\right) + \beta\left(\frac{1}{24} - \sum_{n=1}^{\infty} \frac{2n-1}{e^{(2n-1)\beta}+1}\right) = 0, \ (\alpha\beta = \pi^2) \quad (4.2\,a)$$

As an immediate corollary to (4.2), we have

$$\sum_{n=1}^{\infty} \frac{(2n-1)^{4p+1}}{e^{(2n-1)\pi}+1} = (2^{4p+1}-1)\,\frac{B_{4p+2}}{8p+4}, \ (p = 0, 1, 2 \ldots..) \quad (4.2\,b)$$

Also the limiting form of our result

$$\sum_{n=1}^{\infty} (2n-1)^{4p-1}\left[\frac{\left(\frac{a}{b}\right)^{2p}}{e^{(2n-1)\left(\frac{a}{b}\right)}+1} - \frac{\left(\frac{b}{a}\right)^{2p}}{e^{(2n-1)\pi\left(\frac{b}{a}\right)}+1}\right]$$

$$= (2^{4p-1}-1)\,\frac{B_{4p}}{8p}\left[\left(\frac{b}{a}\right)^{2p} - \left(\frac{a}{b}\right)^{2p}\right], \quad (p = 1, 2, 3, \ldots.),$$

when a and b tend to equality, furnishes the result:

$$\pi \sum_{n=1}^{\infty} (2n-1)^{4p} \operatorname{sech}^2 \frac{(2n-1)\pi}{2} - 8p \sum_{n=1}^{\infty} \frac{(2n-1)^{4p-1}}{e^{(2n-1)\pi}+1} = (2^{4p-1}-1)\,B_{4p},$$

$$(p = 1, 2, 3, \ldots.). \quad (4.2\,c)$$

In conclusion, I wish to thank Prof. B. S. Madhava Rao for the suggestion of the problem and for kind encouragement, and the Government of India for the grant of a Senior Research Scholarship under the Research Training Scheme.

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THE REDOXOKINETIC EFFECT—A GENERAL PHENOMENON

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1. Introduction

Doss and Agarwal[1] discovered that when an alternating field is incident on two platinum electrodes, dipped in an aqueous solution containing quinhydrone, a D.C. potential is developed at each of these electrodes. As this phenomenon is connected with the kinetics of redox processes at the electrodes, the phenomenon has been named "redoxokinetic effect" and the potential is referred to as the "redoxokinetic potential". In the present work a few redox systems have been studied with a view to find out if this is a general phenomenon.

2. Experimental

The circuit diagram used is given in the figure. The alternating current is supplied by a transformer A B and the current is controlled by the rheostat R_1. The electrolytic cell contains three electrodes E_1, E_2 and R. The electrodes E_1 and E_2 conduct the alternating current through the cell. R is the reference electrode, with reference to which the redoxokinetic potential developed at E_1 (the micrc-electrode) is measured. At E_2 the potential developed is small as it is a large electrode and is not normally measured. The potential drop across R_2 is measured by means of the oscillograph, thereby getting an idea of the current passing. The a.c. potential existing between E_1 and R is measured by means of the oscillograph. The d.c. potential (Redoxokinetic potential) developed between E_1 and R is measured by the potentiometer P, making use of the combination of a Macbeth pH meter and a galvanometer, as the null instrument. This combination draws but little current from the system being measured and has high sensitivity. The micro-ammeter M of the Macbeth pH meter was not sufficiently sensitive for our purposes and so we introduced the sensitive galvanometer in series with the micro-ammeter. The key K_1 was closed during the rough adjustment, the final adjustment being done with the key open. The key K_2 in the primary of the transoformer was used for making a.c. on and off.

The experiments were tried with the following redox systems: ferrous-ferric, iodide-iodine, dichromate-chromic and stannous-stannic. With a view to study the effect of concentration and redox ratio (oxidant/reductant ratio) the iodide-iodine system was extensively studied. The results obtained are given in Tables I to VI.

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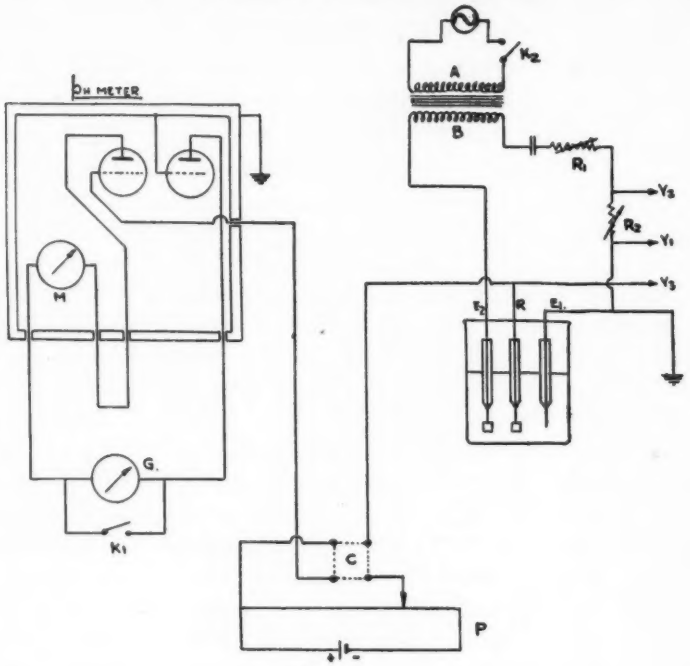

TABLE I

Concentration of ferrous ammonium sulphate .. .. .. 0·25 M
Concentration of ferric sulphate .. .. 0·25 M
Area of the reference electrode and of electrode E_2 each .. .. 2·5 sq. cm.

$V_{max.}$ = a.c. voltage (max.) in volts.
ψ = Redoxokinetic potential in volts.

Serial No.	a.c. current density in milliamps. (max.)/sq. cm. at the micro-electrode	Experiment A		Experiment B	
		$V_{max.}$	ψ	$V_{max.}$	ψ
1	0	0	0	0	0
2	1·8	0·028	−0·0005	0·028	−0·0005
3	3·1	0·038	−0·001	0·037	−0·001
4	6·1	0·057	−0·004	0·055	−0·004
5	10·6	0·081	−0·010	0·080	−0·010
6	14·2	0·099	−0·016	0·099	−0·016
7	19·4	0·112	−0·022	0·113	−0·023
8	28·4	0·140	−0·029	0·141	−0·034
9	39·4	0·194	−0·037	0·194	−0·044

TABLE II

Concentration of potassium dichromate .. .. 0·05 M
Concentration of chromic sulphate .. .. 0·05 M
Area of the reference electrode and of electrode E_2 each .. .. 2·5 sq. cm.

$V_{max.}$ = a.c. voltage (max.) in volts.
ψ = Redoxokinetic potential (in volts).

Serial No.	a.c. current density in milliamps. (max.)/sq. cm. at the micro-electrode	Experiment A		Experiment B	
		$V_{max.}$	ψ	$V_{max.}$	ψ
1	0	0·003	−0·007	0·003	−0·006
2	0·76	0·038	+0·017	0·042	+0·012
3	1·1	0·060	+0·011	0·061	+0·015
4	1·8	0·081	−0·015	0·087	−0·005
5	3·1	0·104	−0·034	0·109	−0·032
6	5·9	0·161	−0·119	0·161	−0·140
7	10·1	0·224	−0·148	0·224	−0·148
8	16·1	0·270	−0·121	0·270	−0·112

TABLE III

Concentration of the stannous chloride .. .. N/5.
Concentration of the stannic chloride .. .. N/5.
Area of the reference electrode and of electrode E_2 each .. .. 2·5 sq. cm.

$V_{max.}$ = a.c. voltage (max.) in volts.
ψ = Redoxokinetic potential in volts.

Serial No.	a.c. current density in milliamps. (max.)/sq. cm. at the micro-electrode	Experiment A		Experiment B	
		$V_{max.}$	ψ	$V_{max.}$	ψ
1	0	0·010	+0·007	0·017	+0·013
2	·37	0·059	−0·008	0·080	−0·006
3	·62	0·087	−0·013	0·108	−0·008
4	·73	0·098	−0·020	0·117	−0·010
5	·83	0·106	−0·022	0·122	−0·011
6	1·0	0·120	−0·012	0·134	−0·001
7	1·6	0·145	+0·039	0·160	+0·041
8	2·4	0·176	+0·065	0·188	+0·081
9	3·9	0·208	+0·088	0·220	+0·117

TABLE IV

Concentration of potassium iodide .. .. 1 N.
Concentration of iodine .. .. N/10.
Area of the reference electrode and of electrode E_2 each .. .. 2·5 sq. cm.

$V_{max.}$ = a.c. voltage (max.) in volts.
ψ = Redoxokinetic potential in volts.

	Experiment A			Experiment B		
Serial No.	a.c. current density in milliamps. (max.)/sq. cm. at the micro-electrode	$V_{max.}$	ψ	a.c. current density in milliamps (r.m.s.)/sq. cm. at the micro-electrode	$V_{max.}$	ψ
1	0	0	0	0	0	0
2	5·9	0·007	0	8·2	0·007	0
3	8·2	0·010	0	10·1	0·008	0
4	10·1	0·012	0	14·2	0·011	0
5	16·5	0·019	+0·001	21·9	0·017	0
6	26·6	0·031	+0·003	35·5	0·028	+0·001
7	30·4	0·036	+0·004	70·9	0·056	+0·002
8	53·2	0·070	+0·013	..	..	..

TABXE V

Concentration of potassium iodide .. .. 1 N.
Concentration of iodine .. .. N/100.
Area of the reference electrode and of electrode E_2 each .. .. 2·5 sq. cm.

$V_{max.}$ = a.c. voltage (max.) in volts.
ψ = Redoxokinetic potential in volts.

Serial No.	a.c. current density in milliamps. (max.)/sq.cm. at the micro-electrode	Experiment A		Experiment B	
		$V_{max.}$	ψ	$V_{max.}$	ψ
1	0	0	0	0	0
2	1·8	0·007	+0·0005	0·007	+0·0005
3	3·0	0·010	+0·001	0·010	+0·001
4	4·4	0·016	+0·003	0·016	+0·002
5	5·9	0·024	+0·006	0·024	+0·006
6	10·1	0·062	+0·026	0·062	+0·027
7	15·3	0·203	+0·153	0·224	+0·179

TABLE VI

Concentration of potassium iodide .. .. 1 N.
Concentration of iodine .. .. N/1000.
Area of the reference electrode and of electrode E_2 each .. .. 2·5 sq. cm.

$V_{max.}$ = a.c. voltage (max.) in volts.
ψ = Redoxokinetic potential in volts.

Serial No.	a.c. current density in milliamps. (max.)/sq. cm. at the micro-electrode	Experiment A		Experiment B	
		$V_{max.}$	ψ	$V_{max.}$	ψ
1	0	0	0	0	0
2	·78	0·003	+0·001	0·003	+0·001
3	1·2	0·010	+0·002	0·010	+0·002
4	1·8	0·018	+0·007	0·018	+0·006
5	3·0	0·037	+0·019	0·039	+0·020
6	5·9	0·143	+0·119	0·170	+0·136
7	10·1	0·241	+0·262	0·246	+0·284

3. DISCUSSION

In the following discussion we will be adopting the American notation, *i.e.*, the sign of the redoxokinetic potential measured is taken as that of the *reference* electrode. Examination of the tables shows that the redoxokinetic effect is a general phenomenon. The nature of the effect however varies with the system. In the ferrous-ferric system, more and more negative redoxokinetic potentials are obtained at higher and higher a.c. fields. In the case of the iodide-iodine system however more and more positive potentials are obtained at higher and higher a.c. fields. The stannous-stannic and dichromate-chromic systems show a d.c. potential even at zero a.c. field which is due to the irreversible nature of the redox systems. These latter systems show a change in the redoxokinetic potential with time and hence the readings were taken after an interval of two minutes after applying the field. There is a certain amount of irregularity in their behaviour, though the general features are reproducible. The results are given in duplicate so as to enable one to judge the reproducibility. It is seen that the reproducibility is good with reversible redox systems. Doss and Agarwal[1] have suggested two working hypotheses for the mechanism of the redoxokinetic effect. According to one of these, the effect is caused by the differential effect of the anodic and cathodic half-wave of the alternating current

on the redoxokinetics. For instance, with the ferrous-ferric system the anodic half-wave may be less effective in bringing about the oxidation of ferrous ions than the cathodic half-wave in bringing about reduction of ferric ions. The result will be a local upsetting of the ratio of the ferric ions to the ferrous ions and the consequent development of the redoxokinetic potential.

According to the second mechanism proposed by Doss and Agarwal[1] a mixture of ferrous and ferric salts in aqueous solution really contains many redox systems such as:—

$$\text{(i)}\ Fe^{++} \rightleftharpoons Fe^{+++} + \Theta$$

$$\text{(ii)}\ \tfrac{1}{2} H_2 \rightleftharpoons H^+ + \Theta$$

$$\text{(iii)}\ OH^- \rightleftharpoons \tfrac{1}{2} H_2O + \tfrac{1}{4} O_2 + \Theta$$

Normally, when the bright platinum electrode is dipped in the mixture of ferrous and ferric salts the three systems interact with each other and undergo chemical transformations such as:—

$$(a)\ Fe^{+++} + \tfrac{1}{2} H_2 \rightleftharpoons Fe^{++} + H^+$$

$$(b)\ Fe^{++} + \tfrac{1}{4} O_2 + \tfrac{1}{2} H_2O \rightleftharpoons Fe^{+++} + OH^-$$

These transformations continue until the activities of H_2 and O_2 at the electrodes conform to a potential equal to the redox potential of the ferrous ferric system. Thus, the well poised redox system controls the potential. The other redox systems which do not have sufficient degree of poise just alter so as to conform to the potential of the well poised redox system. The position, however, changes when an a.c. field is applied. The redox systems tend to respond to the field at any instant; during the cathodic half-wave the reduction reaction, *viz.*, $Fe^{+++} \rightarrow Fe^{++}$, $H^+ \rightarrow H$ and $O_2 \rightarrow OH^-$ take place; during the anodic half-wave, the above reactions get reversed. Of these, the reduction of H^+ or O_2 may be assumed to be taking place at the platinum surface and the ferrous-ferric system only interacts according to the reaction (*a*) and (*b*). These reactions are not equally fast and hence a net-potential results. The results indicate that reaction (*a*) is much faster than reaction (*b*). This can also be expressed by stating that the ferric ion is a better depolariser during the cathodic half-wave than the ferrous ion during the anodic half-wave.

With potassium iodide-iodine systems, the results show that the iodide ion is a better depolariser during the anodic half-wave than iodine during the cathodic half-wave.

In the case of the dichromate-chromic system, it can be easily appreciated, the dichromate ion is an effective depolariser during the cathodic half-

wave, whereas the chromic ion would not be so effective during the anodic half-wave. The electrode would, therefore, tend to get anodically polarised on the whole leading to a highly negative redoxokinetic potential.

The behaviour of the stannous—stannic system, is more complicated. At this stage, the explanation can only be phenomenological. It appears at low potentials, the stannic ion is a better depolariser whereas at high potentials the stannous ion takes the upper hand; the peculiar behaviour may also be due to discharge of stannous ions forming a coating of tin on the electrode.

The data on potassium iodide-iodine systems show that the redox ratio profoundly affects the redoxokinetic potential. It has been pointed out already that the positive values of redoxokinetic potential are caused by the relatively higher depolarising action of iodide ion as compared with iodine itself. Increase of concentration of iodine however, tends to diminish the disparity between the depolarising powers of the oxidant and the reductant, thereby diminishing the magnitude of the redoxokinetic potential.

It is to be pointed out, that though only the second mechanism of Doss and Agarwal has been useful in interpreting much of the data in this paper, the two mechanisms may not be entirely independent. It is indeed likely that the redox systems (ii) and (iii) are even more prone to the unbalanced action of a.c. fields and the reactions (*a*) and (*b*) only modify the potential produced.

The correlation of the a.c. voltage at the micro-electrode with the redoxokinetic potential is difficult at this stage and should await further extensive work on the phenomenon.

4. Acknowledgement

Our thanks are due to Professor J. M. Saha, M.Sc., Director, Indian Institute of Sugar Technology, for his kind interest, Professor K. P. Bhatnagar, M.A., LLB., Principal, D.A.V. College, Kanpur, for kind permission to one of us (H.P.A.) to undertake the investigation at the Indian Institute of Sugar Technology and to the U.P. Scientific Research Committee for a grant which made this work possible.

5. Summary

It has been shown that the redoxokinetic effect is a general phenomenon. The effect of redox ratio on the redoxokinetic potential has been discussed.

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ANALYSIS OF SUGARS AND URONIC ACIDS USING PAPER CHROMATOGRAPHY (HORIZONTAL MIGRATION)

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The qualitative analysis of the common natural sugars by the application of the horizontal migration method of paper chromatography has recently been reported by Rao and Beri.[1] Each sugar, it was shown, has a characteristic circular R_F value by the determination of which the sugar can be identified. This method has now been applied for the separation and identification of glucuronic and galacturonic acids.

These uronic acids, occurring as they do as integral parts of several polysaccharic substances like pectins, gums, mucilages and hemicelluloses, are widely distributed in nature; yet their identification is a matter of some difficulty. The usual method adopted is to convert them into the corresponding dicarboxylic acid, mucic or saccharic acid as the case may be, and identify the latter. During recent years the barium salts of the acids have become handy for identification, for they are shown to have a definite specific rotation. Rarely the uronic acids themselves have been isolated for purposes of identification, since the isolation is somewhat troublesome and takes a long time; sometimes some of their derivatives like phenyl hydrazone and *p*-bromophenyl hydrazone or salts with organic bases like cinchonine and cinchonidine are prepared. All the above methods are either difficult or time-consuming. It has now been found that the identification of the uronic acids can be conveniently effected by employing the horizontal migration method of paper chromatography.

With two-component solvents like moist butanol, moist phenol, moist *s*-collidine, moist *p*-cresol and moist methyl ethyl ketone, the two uronic acids have given almost the same circular R_F values (Table I). These values, which are in general much lower than those of the sugars, may indicate the presence of the uronic acids but are not, on account of overlapping, capable of establishing their individual identity. Hence three-component solvent systems, *viz.*, ethyl acetate-pyridine-water and ethyl acetate-acetic acid-water, which are reported to give good separations in the case of sugars by the solvent-descending method,[2] have been tried, and the results are

presented in Table II. For purposes of comparison the circular R_F values of the sugars and glucurone with the two three-component solvents have also been determined and included in the table. Of the two solvents only one, namely, ethyl acetate-acetic acid-water, has given a good separation of the acids, the circular R_F values for glucuronic and galacturonic acids being 0·17 and 0·30 respectively. However, the value for *d*-galacturonic acid is very close to that of *d*-galactose (0·32), and is, therefore, not capable of distinguishing the uronic acid from the sugar. The differentiation can, however, be easily made by running the chromatogram, also with the second three-component or any of the two-component solvents.

Since the uronic acids are usually isolated as the barium salts, the behaviour of the latter has also been examined. With two-component solvents they have given almost the same circular R_F values (Table I). However, with the three-component solvents their behaviour is different. Each salt has given rise to two rings instead of one, and at present we are not in a position to offer any satisfactory explanation for the appearance of the two rings. The two rings obtained with either of the two three-component solvents are quite characteristic of the salt and enable its identification, when present alone. But, if both the salts are present, the use of ethyl acetate-acetic acid-water as the solvent is not convenient, since both the rings obtained with one salt overlap the corresponding ring of the other salt. With ethyl acetate-pyridine-water, however, it is possible to identify the two uronates even when they are present together. With this solvent, barium glucuronate gives 0·16 and 0·32 for the circular R_F values, while the galacturonate has 0·12 and 0·24 as its values. With a mixture of the two salts, it is possible to get only three rings, since those with the values of 0·12 and 0·16 overlap each other to some extent. However, the rings with the higher values (0·24 and 0·32) are quite distinct and characteristic of the two individual salts.

In the study of natural acid polysaccharides (polyuronides) the paper-chromatographic method of identification of the uronic acids may prove to be quite handy and convenient. The acid hydrolyzate may be neutralized with just the amount of barium hydroxide required for the complete precipitation of sulphuric acid used for the hydrolysis, filtered and the filtrate, which contains sugars and free uronic acid, may be straightaway subjected to paper-chromatographic analysis. As an addition or an alternative, the hydrolyzate may be completely neutralized with barium carbonate, filtered and the filtrate, which contains sugars and barium uronate, may be similarly analyzed using the appropriate solvents,

Experimental

The procedure adopted was just the same as the one already described in our earlier publication (Rao and Beri, *loc. cit.*). With the three-component solvents, however, greater care was found necessary, because slight changes in the relative proportion of the components used to affect the R_F values, as is usual with such systems. In order to keep the composition of the solvent constant right through, firstly the components were taken in exactly measured amounts by means of burette and secondly the evaporation of any of the volatile components was reduced to the minimum by further covering the experimental set-up with another bigger inverted Petri dish. Further, the solvent mixture was prepared only in small amounts so that it was just enough for two or three experiments. It was also found necessary to thoroughly shake the solvent mixture in a separating funnel and allow it sufficient time to attain equilibrium (about half an hour) before it was taken for use. Both with ethyl acetate-pyridine-water and ethyl acetate-acetic acid-water, the lower layer was the discardable aqueous layer and the upper was the solvent mixture for the irrigation of the chromatograms.

Taking Whatman No. 1 circular filter papers (18·5 cm. in diameter) and cutting the tail as described by Rao and Beri (*loc. cit.*), the sugar or the uronic acid solution (1 per cent.) was introduced with the help of a capillary tube as a microdrop at the centre of the filter paper and air-dried. The solvent was taken straight into the Petri dish (15 cm. in diameter) or another small dish placed at its centre in the case of the three-componet solvents, and the filter paper was placed over the Petri dish in the usual way so that the tail hung down into the solvent below. A glass plate was placed over the filter paper and the whole was covered by another inverted bigger Petri dish. The experiments were conducted in a thermostat maintained at 35° C.

When the irrigation was over (30 to 60 minutes depending on the nature of the solvent), the filter paper was removed, the position of the solvent front marked, and dried in an air-oven at 105° for 5 minutes. It was then rapidly and evenly sprayed with a solution of aniline hydrogen phthalate in butyl alcohol and again dried at 105° for 5 minutes. The position taken up by the sugar or the uronic acid was indicated by brown or purplish brown rings. It is worthwhile to note that as a group the pentoses give purplish brown, while the hexoses or the uronic acids derived from them produce brown or dark brown rings, but the shades will be reversed on standing for a few days. By noting the distances through which moved the sugar on the one hand and the solvent on the other, the circular R_F values were calculated as described by Rao and Beri. The values obtained are recorded in the following tables;—

TABLE I

Circular R_F *values at 35° with two-component solvents*

	Moist phenol	Moist *n*-butanol	Moist *s*-collidine	Moist *p*-cresol	Moist methyl ethyl ketone
d-Glucuronic acid (obtained by the hydrolysis of gum arabica)	0·24	0·07	0·19	0·00	0·11
d-Galacturonic acid ..	0·27	0·07	0·16	0·08	0·13
Barium glucuronate ..	0·24	0·07	0·18; 0·28	0·08	0·12
Barium galacturonate ..	0·23	0·07	0·24	0·06	0·10

TABLE II

Circular R_F *values at 35° with three-component solvents*

	Ethyl acetate-pyridine-water (2 : 1 : 2 by volume)	Ethyl acetate-acetic acid-water (3 : 1 : 3 by volume)
d-Glucose ..	0·59	0·36
d-Galactose ..	0·58	0·32
d-Mannose ..	0·70	0·52
d-Fructose ..	0·67	0·57
l-Rhamnose ..	0·81	0·59
d-Arabinose ..	0·66	0·40
d-Xylose ..	0·77	0·57
Lactose ..	0·56	0·24
Maltose ..	0·67	0·26
d-Glucurone ..	0·92	0·63
d-Glucuronic acid ..	0·26	0·17
d-Galacturonic acid ..	0·25	0·30
Barium glucuronate ..	0·16; 0·32	0·17; 0·34
Barium galacturonate ..	0·12; 0·24	0·12; 0·30

SUMMARY

Using the horizontal migration method of filter paper chromatography, the separation and identification of glucuronic and galacturonic acids and their barium salts have been effected.

ACKNOWLEDGEMENT

Our thanks are due to Professor E. L. Hirst, F.R.S., of Edinburgh University, for his valuable criticism and the supply of pure samples of *d*-glucurone and *d*-galacturonic acid.

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PHOTOELASTIC CONSTANTS OF SODIUM CHLORATE FROM ULTRASONIC DIFFRACTION

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1. Introduction

Photoelastic constants are generally measured using a static method (Pockels, 1906). One measures the relative retardation produced in a crystal of known orientation by a known stress, using a Babinet compensator or a similar device. From a study of various sections of the crystal, some of the linear combinations of the piezo-optic constants, q_{ij}, can be obtained. In particular, in cubic crystals belonging to the crystal classes T_d, O and O_h, the quantities $(q_{11} - q_{12})$ and q_{44} are obtained and in those belonging to the classes T and T_h, $(q_{11} - q_{12})$, $(q_{11} - q_{13})$ and q_{44} can be determined. Measurements of absolute path retardation by an interference method are required to obtain all the constants individually. The constants q_{11} and q_{12} in the former type and q_{11}, q_{12} and q_{13} in the latter type of cubic crystals mentioned above can thus be obtained separately from such absolute measurements. The elasto-optic constants, p_{ij}, are calculated from the piezo-optic constants knowing the elastic constants of the crystal. Here also, only certain linear functions of the constants can be obtained from relative measurements and absolute path retardations are required for obtaining them all individually.

The possibility of measuring elasto-optic constants of cubic crystals using ultrasonic diffraction was suggested by Mueller (1938). Here also, it is necessary to measure the absolute amplitude of the ultrasonic wave in the crystal if all the constants are to be obtained independently. But, measurements of the state of polarisation of the diffracted beam in the Hiedemann pattern (1935), for different orientations of the crystal, would enable one to obtain p_{12}/p_{11} and p_{44}/p_{11} for crystal classes T_d, O, O_h and the ratios p_{12}/p_{11}, p_{13}/p_{11} and p_{44}/p_{11} for classes T and T_h. For obtaining these ratios, it is unnecessary to measure the absolute magnitudes of either light or sound intensity.

In both cases, absolute measurements are more difficult than relative measurements. However, absolute data have been obtained with the static

method employing the technique of Pockels (1906), *viz.*, of using two identical plane parallel specimens in a Jamin interferometer, or of Ramachandran (1947), *viz.*, obtaining localised interference fringes between the two surfaces of the crystal; but no absolute measurements appear to have been made by the ultrasonic method.

It is interesting to note that relative measurements made by the static method give *linear functions* of the photoelastic constants, while the ultrasonic method gives *ratios*. Combining the two, therefore, it is possible to get all the constants absolutely. This has, in fact, been done by Burstein, Smith and Henvis (1948) and Vedam (1950) for cubic crystals belonging to the classes T_d, O and O_h and for optical glasses, respectively.

Sodium chlorate belongs to the crystal class T and thus has four piezo-optic constants q_{11}, q_{12}, q_{13}, q_{44} and further exhibits optical activity. By means of special techniques, Ramachandran and Chandrasekharan (1951) measured directly $(q_{11}-q_{12})$, $(q_{11}-q_{13})$ and q_{44}; but they could not make measurements of absolute path retardation. However, they obtained q_{11}, q_{12}, q_{13} separately using ultrasonic data measured by one of us (K. V.) which were made available to them. The present paper deals with the principles, technique and results of the ultrasonic measurements. Both the theory of Mueller and the experimental technique have to be modified to suit the optical activity of sodium chlorate.

2. Theory of the Method

The following theory for a rotating crystal is based on Mueller's results, though we do not follow his conventions regarding signs. It is valid for the case when the ultrasonic amplitude is negligibly small. Consider longitudinal waves being propagated along the [100] or [110] direction in a cubic crystal. In both cases, the direction of vibration is along the direction of propagation. Further, if we consider the ultrasonic diffraction of light incident along the [001] direction on the crystal, then the principal axes of the optical polarisability ellipsoid of the strained crystal are respectively the direction of the light beam, the direction of ultrasonic wave-normal (chosen vertical for convenience), and the third perpendicular direction (horizontal). Denote by A and B, the changes in the optical polarisability in the vertical and horizontal directions. Let $2t$ be the thickness of the crystal and 2α the total optical rotation produced by the crystal. Let light of unit amplitude be incident with its electric vector at an angle $(\theta - \alpha)$ to the horizontal, measured anticlockwise by an observer looking at the source. At a distance x from the centre of the crystal, its azimuth would be $(\theta + x\alpha/t)$. The vertical and horizontal components of the diffracted beam in the first order

produced by a layer dx at x have the amplitudes

$$K\,A \sin(\theta + x\,a/t)\,dx \text{ and } K\,B \cos(\theta + x\,a/t)\,dx,$$

where K is a constant. On emergence, these two components would be

$$K\,[A \sin(\theta + x\,a/t) \cos(t - x)a/t + B \cos(\theta + xa/t)\sin(t - x)a/t]\,dx$$

and $K\,[A \sin(\theta + x\,a/t) \sin(t - x)\,a/t + B \cos(\theta + x\,a/t) \cos(t - x)\,a/t]\,dx$. The total horizontal and vertical components would be given by integrating the above two expressions from $-t$ to $+t$, and their ratio gives cot ϕ where ϕ is the azimuth of the emergent diffracted beam. It is readily shown that

$$\cot\phi = \frac{(A + B)\sin(\theta + a) + (A - B)\sin(\theta - a)\,(\sin 2a)/2a}{(A + B)\cos(\theta + a) - (A - B)\cos(\theta - a)\,(\sin 2a)/2a}.$$

When $a = 0$, *i.e.*, when the crystal is not optically active, $\cot\phi = (B/A)\cot\theta$ from Eq. (1), as is to be expected from Mueller's theory.

The derivation is not rigorous; but it should be accurate enough for the present purpose, since the difference between the cases when rotation is present and when it is absent is only of the order of 2 to 3%, when the ratio A/B or B/A does not exceed 1·5, as is found in the measurements made.

3. Experimental Method

With a non-rotating crystal, the best conditions are obtained when θ is made $\pm 45°$, so that $\tan\phi = A/B$ directly. One measures the angle γ between the plane of vibration of the directly transmitted light and of the light diffracted in the first order. Then $\phi = \theta + \gamma$ and if $\theta = 45°$, $B/A = \cot(45° + \gamma)$.

The same technique can be adopted here also. θ is made equal to 45° and the azimuth of the incident light is made $(\theta - a)$. The rotation $2a$ of the crystal is determined, first of all. The emergent direct light will have an azimuth $(\theta + a)$. and the angle γ between this and the light diffracted in the first order is determined as in the previous case. Then $\phi = (\theta + a + \gamma)$ and in the particular case, it is $= 45° + a + \gamma$.

In the non-rotating case, B/A deviates from cot $(45° + \gamma)$ when the amplitude of the ultrasonic wave is finite. One therefore measures γ for different values of I, the intensity of the ultrasonic beam. Then, plotting cot $(45° + \gamma)$ against I, the value extrapolated to zero I would correspond to B/A (Vedam, 1951). The same technique is adopted here, and if we call the extrapolated value of γ as γ_0 then

$$\phi = 45° + a + \gamma_0.$$

This value of ϕ is put in Eq. (1) and B/A is evaluated.

4. Results of the Measurements

Crystals of sodium chlorate grow readily in the form of rectangular plates with the thickness along one of the cube axes (say [001]) and the length and breadth along [010] and [100] respectively. One such natural crystal was used for the measurement of p_{12}/p_{11} and p_{13}/p_{11} (*cf.* Table I). In another, a face was ground parallel to (110) and it was used for measuring the ratio $(p_{11}+p_{12}-2p_{44})/(p_{11}+p_{12}+2p_{44})$ and thus evaluating p_{44}/p_{11}. The direction of the incident light beam in all cases was along [001]. The direction of the ultrasonic wave-normal, the appropriate ratio B/A and other details are given in Table I. The graphs of cot $(45° + \gamma)$ *vs* I in the three cases are shown in Fig 1.

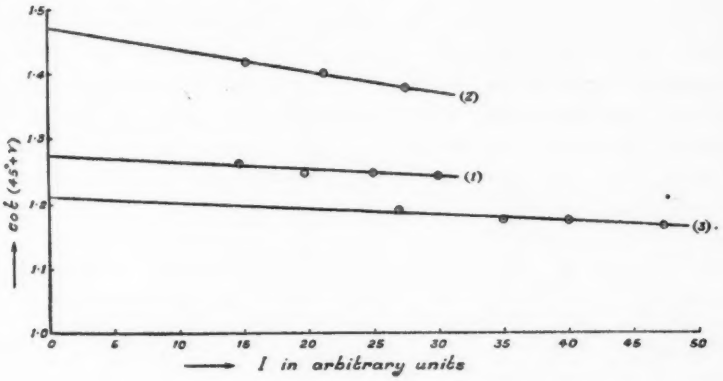

TABLE I

No.	Direction of ultrasonic wave-normal	Theoretical expression for B/A	Measured value of cot $(45°+\gamma)$	2α	B/A from eq. (1)
1	[100]	p_{13}/p_{11}	1·275	20°	1·285
2	[010]	p_{12}/p_{11}	1·47	20°	1·49
3	[110]	$\frac{p_{11}+\frac{1}{2}(p_{12}+p_{13})-2p_{44}}{p_{11}+\frac{1}{2}(p_{12}+p_{13})+2p_{44}}$	1·21	14°	1·215

We thus have

$$p_{12}/p_{11} = 1\cdot49,\ p_{13}/p_{11} = 1\cdot285,\ p_{44}/p_{11} = -0\cdot115.$$

In addition to enabling one to obtain p_{11}, p_{12}, p_{13} separately from measurements of relative retardation, the above ratios are also verified to

be consistent with the measurements of Ramachandran and Chandrasekharan, as will be seen from Table II.

TABLE II

Ratio	Static method	Ultrasonic method
$(p_{11}-p_{12})/(p_{11}-p_{13})$	1·68	1·72
$p_{44}/(p_{11}-p_{12})$ ..	0·22	0·23

SUMMARY

Details are given of the theory and technique of measuring photoelastic constants in optically active cubic crystals from ultrasonic diffraction of light. The results thus obtained, in conjunction with the measurements of relative path retardation produced by stressing the crystal, enable one to obtain all the four constants independently.

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DIAMAGNETISM OF SOME ISOELECTRONIC COMPOUNDS

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Bhatnagar and co-workers[1] extended the Langevin's equation to isoelectronic compounds, containing the same number of atoms, which they termed 'electronic isomers' and obtained the following empirical relation for their molecular susceptibility (χ_m):

$$\chi_m = -2{\cdot}832 \cdot K \cdot r_n^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

in which r_n is the radius of the molecule, calculated according to Bragg's method[2] of the closest packing of atoms and K is a constant for a set of such compounds. They showed that the values of χ_m calculated for a large number of inorganic and organic compounds constituting 'electronic isomers' from the average value of K are in good agreement with the observed values.

In the present paper the validity of the relation I has been tested in the case of (i) $SbCl_3$, TlCNO and (ii) Bi_2O_3 and $SnBr_4$, each set of which separately constitutes isoelectronic compounds containing the same number of atoms. It has been also examined in the case of (i) phenol, aniline, toluene and (ii) *p*-hydroxy phenyl, *p*-aminophenyl and *p*-tolyl arsinic acids. These sets of compounds are separately isoelectronic and contain different numbers of atoms. The nomenclature adopted by Newton Friend[3] for the organo arsenic acids has been used by the author.

Experimental

Most of the substances used were of extrapure quality (Merck's or B.D.H.–A.R. quality). *P*-Hydroxyphenyl and *p*-tolyl arsinic acids were prepared according to the methods described by Bart[4] and Palmer and Adams[5] respectively. A sample of pure *p*-amino phenyl arsinic acid was supplied by Dr. T. N. Ghosh of the Bengal Immunity Research Institute, Calcutta. TlCNO was prepared according to Kuhlmann's method[6] and the purity of these substances was established before use, by standard methods of analysis.

The specific susceptibilities (χ_a) of these compounds are given in -1×10^{-6} cgs. units in column 7 of Table I. Other values are also expressed in the same units. These were measured by means of a modified Gouy's balance in which the usual Paul Bunge balance has been replaced by a Mettler balance, which facilitated the quick weighing of the specimens with the same sensitivity for varying loads. A Mettler balance (semi-micro model) was modified to weigh specimens in and out of a uniform magnetic field as required by the theory of the method. The modifications are shown schematically in Fig. 1 and consist essentially in attaching a pyrex glass fibre assembly to the pan of the balance so as to take up the specimen tube at its lower end.

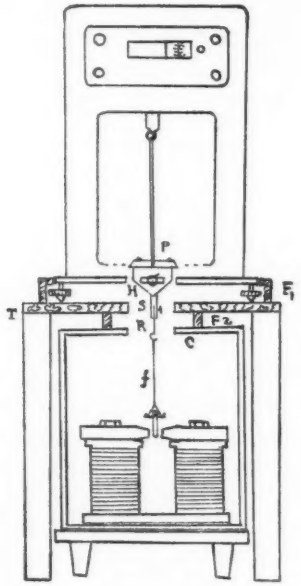

FIG. 1. *P* — Pan ; *H* — Chromium plated Brass Hook ; *S* — Sleeve with side screw ; *R* — Short Aluminium Rod ; *f* — Pyrex glass fibre ; *c* — Magnet casing ; F_1 & F_2 — Wooden frames to prevent wind disturbances ; *T* — Marble Top resting on masonry-pillars.

The gravity and equilibrium nuts on the beam of the balance were adjusted for the sensitivity of the balance and to compensate for the extra weight of the attachment. The electromagnet and the specimen tubes, described by Prasad, Dharmatti and Gokhale[7] were used by the author.

The zero reading on the optical scale of the balance was checked and adjusted, if necessary, before each weighing. The empty clean specimen

tube was weighed and the current was switched on while the beam was fully released and the shift, *i.e.*, the decrease in the weight of the tube was determined. The current was switched off and the initial weight of the tube was checked. The weights and shifts of conductivity water ($\chi_a = 0{\cdot}720$) and KCl-A.R. quality ($\chi_a = 0{\cdot}516$) used as the substances of reference for liquids and solids respectively, and of other substances filled in the specimen tube upto an etched mark were determined in the same manner. Packings of solids varying by 3% of their weight were rejected. The actual weight of the substances and the shifts of the order of a few milligrams were measured with an accuracy of $\pm 0{\cdot}02$ mgm.

The specific susceptibilities of benzene, cyclohexane, sodium chloride and potassium persulphate of extra pure quality were found to be 0·7020, 0·8001, 0·5080 and 0·3746 respectively. The values agree closely with the values reported in literature by previous workers.[8] A number of determinations of the susceptibilities of standard substances of extra pure quality showed that these measurements could be made with an accuracy of $\pm$ 1% with this balance.

Discussion of Results

The specific susceptibilities found by the author for $SbCl_3$, Bi_2O_3, $SnBr_4$, $C_6H_5.OH$, $C_6H_5.NH_2$ and $C_6H_5{\cdot}CH_3$ are in good agreement with those reported in the International Critical Tables and by other workers. The value for TlCNO is in close agreement with the value reported by Trew[9] but is higher than that of Nevgi.[10]

The radii r_n in Å units of the molecules of the several compounds have been calculated according to the method followed by Bhatnagar and co-workers[1] using the latest data of Pauling[11] for the radii of the individual atoms and are given in column 4 of the table. According to Pauling,[11] the single bond covalent radii are so chosen that their sums represent internuclear distances for bonded atoms in molecules and crystals and these are applicable to covalent bonds with considerable ionic character.

The values of K have been calculated from equation I from the observed molecular susceptibilities χ_m, and are given with the mean values for the isoelectronic organic compounds in columns 5 and 6 respectively. The values of χ_m calculated therefrom are given in column 9 of the table.

It will be seen from the table that values of K vary widely in each set of the inorganic compounds and as such a mean value of K cannot be obtained to satisfy relation I. This observation is in line with that of Prasad and co-workers,[7] who found that in several sets of isoelectronic compounds,

containing the same number of atoms, the relation does not hold. This may be due to the fact that in extending the Langevin's equation of a monatomic system to a polyatomic one, Bhatnagar and co-workers[1] did not take into account factors, such as the nature of the chemical binding existing in the molecules and the differences in the solid and liquid states of the inorganic compounds.

The only remarkable feature of their relation appears to be its applicability to isoelectronic organic compounds. It is seen from Table I that the values of K are nearly the same in each set of the organic compounds. The values of χ_m, calculated from the corresponding average values of K are in good agreement with the observed ones.

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TABLE I

Substances	No. of atoms	No. of electrons	r_n Å units	K	Mean K	χa	χm	χm cal
(i) $SbCl_3$ ..	4	102	1·787	9·183	..	0·3640	83·03	..
TlCNO ..	4	102	1·621	7·454	..	0·2251	55·46	..
(ii) Bi_2O_3 ..	5	190	1·921	7·670	..	0·1700	80·15	..
$SnBr_4$ ..	5	190	2·054	12·990	..	0·3542	155·20	..
(i) C_6H_5OH ..	13	50	1·473	9·91	10·193	0·6480	60·91	62·59
$C_6H_5NH_2$ ..	14	50	1·486	10·24		0·6890	64·08	63·72
$C_6H_5CH_3$ ..	15	50	1·507	10·43		0·7119	67·08	65·51
(ii)								
p-HO.C_6H_4.As : $O(OH)_2$	18	108	1·803	12·36	12·56	0·5390	113·80	115·60
p-$H_2N.C_6H_4$.As : $O(OH)_2$	19	108	1·811	12·61		0·5560	117·10	116·60
p-$H_3C.C_6H_4$.As : $O(OH)_2$	20	108	1·826	12·71		0·5400	120·00	118·60

SUMMARY

The magnetic susceptibilities of (*a*) isoelectronic compounds containing the same number of atoms such as (i) $SbCl_3$, TlCNO; (ii) Bi_2O_3, $SnBr_4$ and (*b*) of isolectronic compounds containing different number of atoms, such as (i) phenol, aniline, toluene and (ii) *p*-hydroxyphenyl, *p*-aminophenyl, *p*-tolyl arsinic acids were measured on a new type of Gouy's balance in which a modified Mettler balance has been employed. The essential modifications have been indicated.

The validity of the empirical relation $\chi_m = -2{\cdot}832.K.r_n^2$ deduced by Bhatnagar and co-workers for isoelectronic compounds with the same number of atoms, has been examined in the case of the above compounds. It has been shown that the relation, does not apply to the inorganic compounds belonging to category (*a*) but applies to the organic compounds belonging to category (*b*).

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FIXED CONFIGURATIONS OF FOUR RECTILINEAR VORTEX FILAMENTS

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§1. Introduction

The problem of the motion of three parallel rectilinear vortex filaments of strengths K_1, K_2, K_3 in a perfect incompressible fluid extending to infinity originally considered by Gröbli [1877] has been subjected to a thorough investigation by Synge [1949] in a recent paper. He has classified all possible motions by representing them by trilinear co-ordinates, and this elegant method of studying the changes in configuration by curves in the representative space yields interesting information on the types of motion, and on the stability of fixed configurations. It may also be mentioned here that the particular result obtained by Synge of the equilateral configuration being stable for small displacements when $K_2K_3 + K_3K_1 + K_1K_2 > 0$ had previously been noticed by Morton [1934]. He obtained this condition in the form that, for stability, the mean-centre of the vortices should lie inside the circum-circle of the triangle, and it is easily deduced that this is equivalent to the above inequality.

The corresponding problem of determining all possible types of motion in the case of four vortices is rather complicated on account of the very large number of such types, and the inadequacy of the geometrical representation of configurations by tetrahedral co-ordinates, which cannot distinguish, for example, a square from a rhombus. As a first step, we have discussed in this paper possible types of *fixed* configurations of four vortices, *i.e.*, those with sides and diagonals of fixed lengths throughout the motion, but without regard to rigid body displacements of that figure. We have also indicated some particular distributions of the four vortex strengths K_1, K_2, K_3, K_4 which ensure the invariance of *form* of special configurations.

§2. Basic Equations

Let the vortices of strengths K_1, K_2, K_3, K_4 be situated at the points A, B, C, D (Fig. 1) and let the sides and diagonals BC, CA, AB, AD, BD, CD be denoted by a, b, c, f, g, h respectively. In accordance with the

usual convention, we regard a strength as positive when it gives a counter-clockwise circulation. Consider the rate of increase a' of the side $BC = a$. The motions due to the vortices K_2 and K_3 at its extremities contribute nothing to a' and the rate of change of a can arise only from the motions of the vortices K_1 and K_4. The end B has due to K_1 and K_4 velocities of magnitude $\frac{K_1}{c}$ and $\frac{K_4}{g}$ perpendicular to AB and BD respectively; similarly the end C has due to these same K_1 and K_4, velocities $\frac{K_1}{b}$ and $\frac{K_4}{g}$ perpendicular to CA and CD respectively. Reference to Fig. 1 now shows that

$$a' = \frac{K_1}{b}\sin \mathrm{BCA} - \frac{K_1}{c}\sin \mathrm{ABC} + \frac{K_4}{h}\sin \mathrm{BCD} - \frac{K_4}{g}\sin \mathrm{DBC}$$

or,

$$\tfrac{1}{2}aa' = K_1\left(\frac{1}{b^2} - \frac{1}{c^2}\right)\Delta\,\mathrm{ABC} - K_4\left(\frac{1}{g^2} - \frac{1}{h^2}\right)\Delta\,\mathrm{BCD}.$$

Denoting the circum-radii of triangles BCD, CDA, DAB and ABC by R_1, R_2, R_3 and R_4 respectively, we can write the above as

$$2R_1R_4a' = K_1R_1\left(\frac{c}{b} - \frac{b}{c}\right) - K_4R_4\left(\frac{h}{g} - \frac{g}{h}\right).$$

We can similarly determine b', c', f', g', h' and write the basic equations in the following form:

$$\left.\begin{aligned}
2R_1R_4a' &= K_1R_1\left(\frac{c}{b} - \frac{b}{c}\right) - K_4R_4\left(\frac{h}{g} - \frac{g}{h}\right)\\
2R_2R_4b' &= K_2R_2\left(\frac{a}{c} - \frac{c}{a}\right) - K_4R_4\left(\frac{h}{f} - \frac{f}{h}\right)\\
2R_3R_4c' &= K_3R_3\left(\frac{b}{a} - \frac{a}{b}\right) - K_4R_4\left(\frac{g}{f} - \frac{f}{g}\right)\\
2R_2R_3f' &= K_2R_2\left(\frac{c}{g} - \frac{g}{c}\right) - K_3R_3\left(\frac{h}{b} - \frac{b}{h}\right)\\
2R_3R_1g' &= K_3R_3\left(\frac{h}{a} - \frac{a}{h}\right) - K_1R_1\left(\frac{f}{c} - \frac{c}{f}\right)\\
2R_1R_2h' &= K_1R_1\left(\frac{b}{f} - \frac{f}{b}\right) - K_2R_2\left(\frac{g}{a} - \frac{a}{g}\right)
\end{aligned}\right\}\quad (2\cdot1) - (2\cdot6).$$

In order that the configuration be fixed, it is *sufficient* that the six equations

$$a' = b' = c' = f' = g' = h' = 0 \qquad (2\cdot7)$$

should hold: but all the six of (2·7) cannot however be independent, in view of the identical relation connecting the six distances between any four

points in a plane. Using (2·7) the conditions of fixed configurations can be written as

$$\left.\begin{aligned}
K_1R_1\left(\frac{c}{b}-\frac{b}{c}\right) &= K_4R_4\left(\frac{h}{g}-\frac{g}{h}\right)\\
K_2R_2\left(\frac{a}{c}-\frac{c}{a}\right) &= K_4R_4\left(\frac{h}{f}-\frac{f}{h}\right)\\
K_3R_3\left(\frac{b}{a}-\frac{a}{b}\right) &= K_4R_4\left(\frac{g}{f}-\frac{f}{g}\right)\\
K_2R_2\left(\frac{c}{g}-\frac{g}{c}\right) &= K_3R_3\left(\frac{h}{b}-\frac{b}{h}\right)\\
K_3R_3\left(\frac{h}{a}-\frac{a}{h}\right) &= K_1R_1\left(\frac{f}{c}-\frac{c}{f}\right)\\
K_1R_1\left(\frac{b}{f}-\frac{f}{b}\right) &= K_2R_2\left(\frac{g}{a}-\frac{a}{g}\right)
\end{aligned}\right\} \quad (2\cdot8)-(2\cdot13)$$

Since the vortex strengths appear in the combinations K_1R_1, K_2R_2, K_3R_3 and K_4R_4 in the above relations, we can easily find all possible relations between a, b, c, f, g, h that can be deduced from the above by eliminating the vortex strengths. Remarkably enough, all these relations reduce to one and the same equation given by

$$\begin{vmatrix} 1 & 1 & 1 \\ a^2+f^2 & b^2+g^2 & c^2+h^2 \\ a^2f^2 & b^2g^2 & c^2h^2 \end{vmatrix} = 0 \qquad (2\cdot14)$$

As mentioned above the six relations (2·8)-(2·13) cannot all be independent. In fact, it can be shown that from any four of these relations, the remaining two can be deduced. Alternatively, using (2·14) and three suitably chosen relations from (2·8)-(2·13) the remaining three can also be deduced. Thus any *four* relations of the above constitute a set of necessary and sufficient conditions for fixed configurations. Equation (2·14) might be interpreted as a necessary geometrical condition (*i.e.*, not involving the vortex strengths) for the configuration being fixed. Having now established the consistency of the conditions (2·8)-(2·13), we can use them to investigate particular symmetrical configurations.

It can be easily verified that our basic equations (2·1)-(2·6) satisfy the usual Kirchhoff's Integrals of the motion of a system of rectilinear vortex filaments, *viz.*,

$$(a)\ \Sigma' K_mK_n \log r_{mn} = \text{constant.}$$

$$(b)\ \Sigma\ K_m r_m^2 = \text{constant.}$$

§3. Particular Configurations

While any four equatinos of (2·8)–(2·13) specify general quadrilateral configurations, we will now consider special forms and determine what distribution of vortex strengths will ensure fixed configurations in these special cases.

Case 1: *Square*

Here, $a=c=f=h$, $b=g$, $R_1=R_2=R_3=R_4$. Equations (2·8), (2·10) and (2·11) give as $K_1=K_4$, $K_3=K_4$, and $K_2=K_3$ respectively and the other equations hold under these conditions.

Hence we have the result:

(i) *Vortices at the corners of a square can remain as a fixed configuration with the strengths of all the vortices equal.*

Case 2: *Rhombus*

Here $a=c=f=h$, $b\neq g$, $R_1=R_3$, $R_2=R_4$.

Equations (2·8) and (2·10) on division lead to $K_1=K_3$.

Similarly equations (2·10) and (2·11) give us $K_2=K_4$.

Then equation (2·8) can be written as

$$K_1R_1\frac{b^2-a^2}{b}=K_2R_2\frac{g^2-a^2}{g}$$

Writing

$$R_1=a/2\sin\alpha,\ R_2=a/2\cos\alpha,$$
$$g=2a\cos\alpha,\quad b=2a\sin\alpha$$

this simplifies to

$$K_1\cos^2\alpha(4\sin^2\alpha-1)=K_2\sin^2\alpha(4\cos^2\alpha-1) \tag{3·1}$$

or

$$\frac{K_1}{K_2}=-\tan\alpha\tan 3\alpha. \tag{3·1*}$$

Hence we have the result:

(ii) *Vortices at the corners of a rhombus can remain in a fixed configuration with the strengths of the vortices at the extremities of the same diagonal equal. These distinct vortex strengths are connected by equation* (3·1) *or* (3·1*).

As shown by (3·1*) the value $\alpha=\frac{\pi}{6}$ is forbidden since it makes $\frac{K_1}{K_2}$ infinite. Thus four vortices forming a rhombus with three of them at the corners of an equilateral triangle cannot remain fixed. We shall come back to the consideration of such fixed configurations in the next section.

CASE 3: *Rectangle*

Here $a=f,\ b=g,\ c=h,\ R_1=R_2=R_3=R_4$.

Equation (2·14) gives us in this case

$$2a^2(b^4-c^4)+2b^2(c^4-a^4)+2c^2(a^4-b^4)=0,$$

i.e.,
$$(a^2-b^2)(b^2-c^2)(c^2-a^2)=0,$$

i.e., $c=a$ or the rectangle is a square, which is Case 1.

Hence we have the result:

(iii) *Four vortices at the corners of a rectangle cannot remain in a fixed configuration.*

Also equations (2·8), (2·9), (2·10) and (2·11) give us $K_1=K_4$, $K_2=-K_4$, $K_3=K_4$ and $K_2=K_3$ respectively, which are not compatible, thus confirming the above result.

CASE 4: *Parallelogram*

Here $a=f,\ b\neq g,\ c=h,\ R_1=R_3,\ R_2=R_4$.

Equations (2·9) and (2·12) give us $K_2=-K_4$, $K_1=-K_3$.

Equations (2·8) and (2·10) give then, on division,

$$\frac{K_1R_1(c^2-b^2)/bc}{K_3R_3(b^2-a^2)/ab}=\frac{K_4R_4(h^2-g^2)/gh}{K_4R_4(g^2-f^2)/fg}$$

Using that

$$b^2=a^2+c^2-2ac\cos\theta,$$

$$g^2=a^2+c^2+2ac\cos\theta$$

$$\frac{a(a^2-2ac\cos\theta)}{c(c^2-2ac\cos\theta)}=-\frac{a(a^2+2ac\cos\theta)}{c(c^2+2ac\cos\theta)}$$

which gives $4\cos^2\theta=1$ leading to $\theta=60°$. It is easily verified that this also follows from (2·14). Further (2·8) gives

$$\frac{K_1}{K_2}=-\frac{K_1}{K_4}=\frac{R_4(g^2-h^2)/gh}{R_1(c^2-b^2)/bc}$$

$$=-\frac{(b/2\sin\theta)(a^2+ac)b}{(g/2\sin\theta)(a^2-ac)g}$$

$$=-\frac{(a^2+c^2-ac)(a+c)}{(a^2+c^2+ac)(a-c)}$$

$$=\frac{c^3+a^3}{c^3-a^3}$$

$$\frac{K_1}{K_2}=\frac{c^3+a^3}{c^3-a^3} \qquad (3\cdot2)$$

Hence we have the result:

(iv) *A parallelogram of vortices can remain in a fixed configuration when the angle of the parallelogram is $\pi/3$ and the vortices at the ends of the diagonals are equal in magnitude but opposite in sense. Also the two distinct vortex strengths are connected as in equation* (3·2).

It is worthy of note that the angle exlcuded in the rhombus is the one which is necessary in this case.

CASE 5: *Two isosceles triangles on a common base forming a lozenge.*

In Fig. 6 (*a*), $a=c$, $f=h$, $R_1=R_3$.

Then equation (2·12) gives us $K_1=K_3$.

Equations (2·8) and (2·11) then give us

$$K_1R_1\left(\frac{a}{b}-\frac{b}{a}\right)=K_4R_4\left(\frac{f}{g}-\frac{g}{f}\right) \tag{3·3a}$$

$$K_1R_1\left(\frac{f}{b}-\frac{b}{f}\right)=K_2R_2\left(\frac{a}{g}-\frac{g}{a}\right) \tag{4·4a}$$

Writing

$$b=2a\sin\alpha=2f\sin\beta$$

$$g=a\cos\alpha+f\cos\beta$$

$$R_2=b/2\sin 2\beta,\ R_4=b/2\sin 2\alpha,\ R_1=\frac{a}{2\sin\beta}=\frac{f}{2\sin\alpha}$$

these two equations simplify to

$$K_1\cos\alpha\sin(\alpha+\beta)(1-4\sin^2\alpha)=2K_4\sin\beta[\sin^2\alpha-\sin^2(\alpha+\beta)] \tag{3·3a^x}$$

$$K_1\cos\beta\sin(\alpha+\beta)(1-4\sin^2\beta)=2K_2\sin\alpha[\sin^2\beta-\sin^2(\alpha+\beta)] \tag{3·4a^x}$$

and on division we have

$$K_2\sin 2\alpha(1-4\sin^2\alpha)[\sin^2\beta-\sin^2(\alpha+\beta)]$$
$$=K_4\sin 2\beta(1-4\sin^2\beta)[\sin^2\alpha-\sin^2(\alpha+\beta)] \tag{3·5a}$$

In Fig. 6 (*b*), we have $c=f$, $a=h$, $R_2=R_4$.

Then equation (2·9) gives us $K_2=K_4$. In the same way as in Fig. 6 (*a*) we have the relations

$$K_2R_2\left(\frac{c}{g}-\frac{g}{c}\right)=K_3R_3\left(\frac{a}{b}-\frac{b}{a}\right) \tag{3·3b}$$

$$K_1R_1\left(\frac{b}{c}-\frac{c}{b}\right)=K_2R_2\left(\frac{g}{a}-\frac{a}{g}\right) \tag{3·4b}$$

These lead to

$$K_2\cos\alpha\sin(\alpha+\beta)(1-4\sin^2\alpha)=2K_3\sin\beta[\sin^2\alpha-\sin^2(\alpha+\beta)] \tag{3·3b^x}$$

$$K_2 \cos\beta \sin(\alpha+\beta)(1-4\sin^2\beta) = 2K_1 \sin\alpha [\sin^2\beta - \sin^2(\alpha+\beta)] \quad (3\cdot4b^x)$$

and on division

$$K_1 \sin 2\alpha (1-4\sin^2\alpha)[\sin^2\beta - \sin^2(\alpha+\beta)]$$
$$= K_3 \sin 2\beta (1-4\sin^2\beta)[\sin^2\alpha - \sin^2(\alpha+\beta)] \quad (3\cdot5b)$$

(the same relations as before) with reference to the new figure.

Hence we have the result:

(v) *Vortices at the extremities of a lozenge can remain in a fixed configuration with the vortices at the extremities of the common base having the same strength. The strengths of these and the remaining two are connected by the relations* (3·3a*), (3·4a*), (3·5 a).

As shown by (3·3a*) or (3·4a*) the values $\alpha = \frac{\pi}{6}$, $\beta = \frac{\pi}{6}$ are forbidden as these make the ratios $\frac{K_1}{K_4}$ and $\frac{K_1}{K_2}$ infinite. This is in conformity with the remark made in the case of the rhombus.

CASE 6: *Isosceles Trapezium*

In the first case

$$c=h,\ b=g,\ R_1=R_2=R_3=R_4.$$

Equations (2·8) and (2·11) lead to $K_1=K_4$, $K_2=K_3$. In the second case $a=f$, $b=g$, $R_1=R_2=R_3=R_4$ and equations (2·10), (2·13) lead to $K_3=K_4$, $K_1=K_2$. Confining ourselves to the first of the two figures, equations (2·9), (2·10) give us

$$K_2\left(\frac{a}{c}-\frac{c}{a}\right) = K_1\left(\frac{c}{f}-\frac{f}{c}\right) \quad (3\cdot6)$$

$$K_2\left(\frac{b}{a}-\frac{a}{b}\right) = K_1\left(\frac{b}{f}-\frac{f}{b}\right) \quad (3\cdot7)$$

Any one of these equations connect K_1 and K_2. Eliminating K_1 and K_2 between these equations, we get

$$\frac{(a^2-c^2)/ac}{(b^2-a^2)/ab} = \frac{(c^2-f^2)/cf}{(b^2-f^2)/bf}$$

Writing

$$b^2 = c^2 + f^2 + 2cf\cos\theta,$$
$$a^2 = f^2 + 4c^2\cos^2\theta + 4cf\cos\theta,$$

we get

$$\frac{(f^2+4c^2\cos^2\theta+4cf\cos\theta-c^2)}{(c^2-4c^2\cos^2\theta-2cf\cos\theta)} = \frac{c^2-f^2}{c^2+2cf\cos\theta}.$$

Putting $\frac{f}{c} = \lambda$, this leads to

$(\lambda^2 + 2\lambda \cos\theta + 4\cos^2\theta - 1)(1 + 2\lambda\cos\theta) = (1 - 4\cos^2\theta - 2\lambda\cos\theta)(1-\lambda^2)$

i.e., $\lambda^2(1 + 2\cos^2\theta) + 2\lambda\cos\theta(1 + 2\cos^2\theta) - (1 - 4\cos^2\theta) = 0,$

or

$$\lambda^2 + 2\lambda\cos\theta - \frac{1 - 4\cos^2\theta}{1 + 2\cos^2\theta} = 0. \tag{3·8}$$

This equation which also follows from (2·14) prescribes the value of $\frac{f}{c}$. As $\frac{f}{c}$ is essentially real, from equation (3·8) it follows that $\theta \geqslant \frac{\pi}{4}$. Also since $\frac{f}{c}$ is a positive magnitude, $\theta \geqslant \frac{\pi}{3}$. When $\theta = \frac{\pi}{3}$, $\lambda = 0$ and the vortices at A and D combine into a single vortex, the configuration degenerating into an equilateral triangle. The equation (3·6) connecting K_1 and K_2 can be written in terms of λ.

We have

$$K_1/K_2 = \frac{\lambda(\lambda^2 + 4\lambda\cos\theta + 4\cos^2\theta - 1)}{(1 - \lambda^2)(\lambda + 2\cos\theta)} \tag{3·6*}$$

Hence, we have the result:

(vi) *Vortices at the corners of an isosceles trapezium can remain in a fixed configuration with its acute angle* $> \pi/3$ *and with the vortices at the extremities of the parallel sides equal. The two distinct vortex strengths are connected by* (3·6*). *Equation* (3·8) *gives us the ratio between an equal side and one of the parallel sides.*

§4. Degenerate Configurations

We know from Synge's theory of three vortices that the degenerate collinear configuration plays a very important part. In the present case, we have to consider, besides the case of four collinear vortices, also the case where three are collinear and the fourth is outside this line of collinearity. We shall consider the latter case first.

Case 7: *Three out of four vortices, collinear*

With A, B, C collinear and D outside, we have here $b = c + a$ and $R_4 = \infty$ and equations (2·8)–(2·13) lead immediately to the result

$$f = g = h \text{ or, } R_1 = \infty,\ R_2 = \infty,\ R_3 = \infty.$$

i.e., $$f = g = h = 0 \text{ or } R_1 = \infty,\ R_2 = \infty,\ R_3 = \infty.$$

$\therefore$ D is collinear with A, B, C.

Hence, we have the result:

(vii) *Three collinear vortices along with another cannot form a fixed configuration, unless all the four are collinear.*

CASE 8: *Three vortices forming an equilateral triangle along with a fourth vortex.*

Let us consider the case where the quadrilateral formed by the vortices is a re-entrant one. In this case we can use the same general equations with the modification necessary to allow for the fact that one of the vortices is inside the triangle formed by the other three. Thus, for example, when D (K_4) is inside the triangle ABC, we have to take the sign of the area ADC in Fig. 9 negative.

We can accordingly rewrite our equations (2·8)-(2·13) by replacing R_2 by $-R_2$. If we postulate that triangle ABC is equilateral, *i.e.*, $a=b=c$, the above equations yield $g=h=f$ or $R_1, R_2, R_3=\infty$. The latter alternative means that D, B, C are collinear and A is outside the line of collinearity. But from result (vii), we see that such a fixed configuration is not possible. Therefore, $g=h=f$, *i.e.*, D is the centre of the equilateral triangle ABC. Further, the same equations yield $K_1=K_2=K_3$.

Hence, we have the result:

(viii) *Three vortices forming an equilateral triangle can form a fixed configuration along with a fourth vortex, if and only if, the strengths of the vortices at the corners of the equilateral traingle are equal and the fourth vortex (strength* $\neq 0$*) lies at the centre of the equilateral triangle.*

This result is in consonance with the particular cases considered under the rhombus and the lozenge.

CASE 9: *Four collinear vortices*

In this degenerate case the equations (2·8)-(2·13) are identically satisfied in view of $R_1, R_2, R_3, R_4=\infty$. We, therefore ,derive *ab initio*, the fundamental equations suitable for this case.

Let the vortices K_1, K_2, K_3, K_4 at A, B, C, D be collinear at time $t=0$. Let c, a, h denote the distances AB, BC, CD respectively. We can easily calculate the velocities of each of A, B, C, D due to the other three vortices perpendicular to the line of collinearity and determine their positions A′, B′, C′, D′ after time t. Expressing the conditions that these four points are collinear, we have the equations

$$\left.\begin{aligned}&\frac{K_1+K_2}{c^2}-\frac{K_3}{a(a+c)}-\frac{K_4}{(a+h)(a+c+h)}\\&=-\frac{K_1}{c(a+c)}+\frac{K_2+K_3}{a^2}-\frac{K_4}{h(a+h)}\\&=-\frac{K_1}{(a+c)(a+c+h)}-\frac{K_2}{a(a+h)}+\frac{K_3+K_4}{h^2}.\end{aligned}\right\}\ (4\cdot1)-(4\cdot2)$$

It is hardly necessary to verify directly that the lengths c, a, h remain invariant for it follows from equations (2·1)-(2·6) that $R_1=R_2=R_3=R_4=\infty$ leads to

$$a'=b'=c'=f'=g'=h'=0.$$

Equations (4·1) and (4·2) are not in a particularly elegant form. But we can examine suitable particular collinear configurations for fixity. Allowing for negative strengths of the vortices we examine the cases

$$K_1=-K_2=-K_3=\ K_4,$$
$$K_1=-K_2=\ K_3=-K_4,$$
$$K_1=\ K_2=-K_3=-K_4.$$

and find that they cannot constitute a fixed configuration.

In the other symmetrical cases

(*a*) $K_1=K_4,\ K_2=K_3$;

(*b*) $K_1=K_3,\ K_2=K_4$;

(*c*) $K_1=K_2,\ K_3=K_4$;

equations (4·1), (4·2) show the possibility of such configurations without, however, yielding results in any elegant form except in the case (*a*), where we have $c=h$ as a possible alternative.

A further particular case of (*a*) with the highest order of symmetry is obviously the case where $K_1=K_2=K_3=K_4$ and this gives $c=h$ and that $\frac{a}{c}$ satisfies the equation

$$x^4+4x^3+2x^2-4x-2=0 \qquad (4\cdot3)$$

From the usual conditions for the reality of the roots of a biquadratic, it follows that equation (4·3) has all its roots real and further an immediate application of Descartes' Rule of Signs indicates that it has one and only one positive root. $\frac{a}{c}$ is obviously this positive root.

A numerical solution of (4·3) using the Horner's Method gives its root $\alpha_0=0\cdot932$.

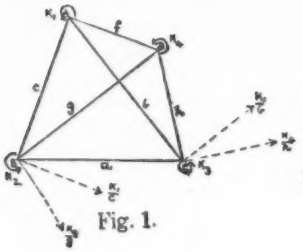

Fig. 1.

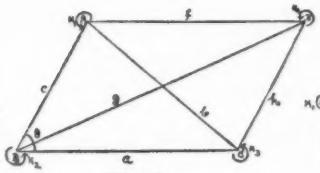

Fig. 5.

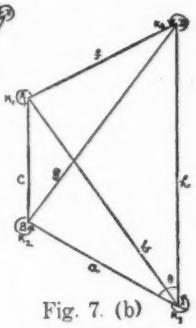

Fig. 7. (b)

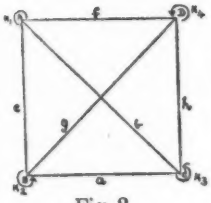

Fig. 2.

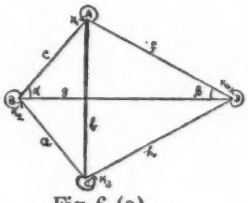

Fig. 6. (a)

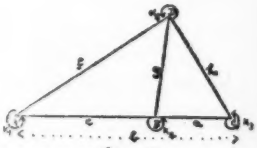

Fig. 8.

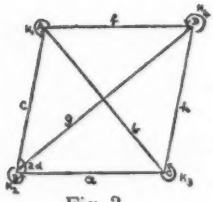

Fig. 3.

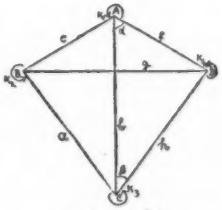

Fig. 6. (b)

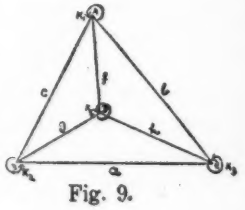

Fig. 9.

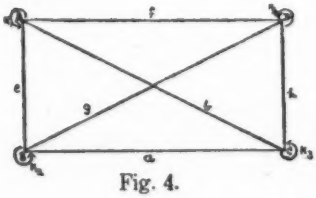

Fig. 4.

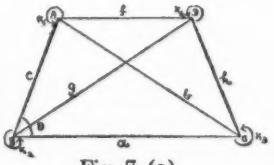

Fig. 7. (a)

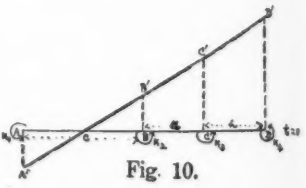

Fig. 10.

FIGS. 1-10

Hence, we have the result:

(ix) *Collinear vortices of equal strength separated by distances proportional to* 1, a_0, 1 *can form a fixed configuration.*

§5. Configurations with Invariant Form

In the case of a parallelogram, we have deduced in (iv) that for a fixed configuration one of the angles of the parallelogram should be 60° and the strengths of the vortices at the diagonally opposite points should be equal and opposite in sign. It has however been shown by D. Gorjatschoff [1898] that any parallelogram with vortices at the ends of the diagonals of equal strength moves such that the vortices at the end of any time, again form a parallelogram. This is obvious since, taking the original position of the mean centre as origin, the position vectors at any time should satisfy the equation

$$K_1(\vec{r_1}+\vec{r_3})+K_2(\vec{r_2}+\vec{r_4})=0 \qquad (5\cdot1)$$

K_1 and K_2 the equal vortex strengths at the ends of the diagonals, being arbitrary (5·1) leads to

$$\vec{r_1}+\vec{r_3}=0,\ \vec{r_2}+\vec{r_4}=0$$

i.e., the extremities of the vectors again form a parallelogram. We wish to derive other results of a similar type. In the case of a rectangle, we know that [Lamb, (1945)] the form is conserved for the distribution of vortices k, k at the ends of one diagonal and $-k$, $-k$ at the ends of the other. This can be easily verified by using the relation §2 (*b*). This distribution of vortices obviously satisfies what is assumed above in the case of the parallelogram. This therefore, ensures the conservation of the parallelogram form. Further, the relation §2 (*b*), *viz.*, $\Sigma K_m r_m^2 = \text{constant}$ gives $r_1^2 - r_2^2 + r_3^2 - r_4^2 = 0$, since the constant is initially equal to zero. Conservation of the parallelogram form gives $r_1 = r_3$, $r_2 = r_4$. Hence $r_1 = r_2$, *i.e.*, the diagonals are equal, *i.e.*, the rectangle form is conserved.

We will now consider the rhombus configuration and show that in general (*i.e.*, with $K_1 = K_3$, $K_2 = K_4$) the form cannot be conserved. For this, we take the simplest possible case where all the vortices are of equal strength and show that even here, the rhombus form cannot be conserved. Equation §2 (*b*) gives the constant involved equal to $2ka_0^2$, where a_0 is the side of the initial rhombus, and k the common strength of the four vortices. Hence at any time one should have $2K(r_1^2 + r_2^2) = 2Ka_0^2$, *i.e.*, $r_1^2 + r_2^2 = a_0^2$. This requires, if the rhombus form is to be conserved, that its side should

always be equal to a_0; in other words, the configuration is a fixed one. Hence, we have the result:

A rhombus cannot retain its form unless it be a fixed configuration.

I wish to thank Professor B. S. Madhava Rao for kindly suggesting the problem and for helpful guidance.

Summary

For the case of the motion of four rectilinear vortex filaments, the rates of change of the sides and diagonals of the quadrilateral formed by them have been derived, and these results are used to investigate various possible cases of *fixed* configurations formed by the four vortices.

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THE THEORY OF REDOXOKINETIC EFFECT AND A GENERAL METHOD FOR THE DETERMINATION OF "a" OF ABSOLUTE REACTION RATES

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1. Introduction

When two platinum electrodes dipped in an aqueous solution are connected to a source of alternating current, it is found that a d.c. potential is developed at each of the electrodes. This d.c. potential can be measured with reference to a third platinum electrode of large area dipped in the same solution. This phenomenon which is caused by the kinetic factors controlling oxidation and reduction reactions at the electrodes has been termed the "Redoxokinetic Effect." The experimental set-up for the study of the phenomenon and some of the results obtained have been already published.[1,2] It is the object of the present work to formulate a theory to explain quantitatively the phenomenon. An allied problem has been tackled by Randles.[3] His procedure has been modified in the present work, taking into account the redoxokinetic effect.

2. Theoretical

Consider a microelectrode dipped in a mixture of an oxidant and a reductant, *e.g.*, ferrous and ferric ions in equal proportions and in small concentrations (of the order of a few millimoles per litre). Let the concentration of each be C moles per c.cm. The solution also contains a supporting indifferent electrolyte at a high concentration so as to avoid the migration effects. Let this electrode be subjected to the action of a small alternating electric field with the help of another platinum electrode dipped in the solution. A third dummy electrode of large area is also kept in solution with a view to use it as a reference electrode for the measurements of the potentials. We may now consider the reaction occurring at the microelectrode due to the electric field which can be represented by the equation:—

$$M^{n+} + ne \rightleftarrows M^{(n-n)+}. \qquad (1)$$

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Since no current is passing through the dummy electrode, the reaction (1) is in equilibrium at this electrode, we shall take the potential of the dummy electrode arbitrarily as zero. The potential v, of the microelectrode with reference to the dummy electrode is given by the equation:—

$$v = V \cos \omega t + \psi, \tag{2}$$

where the first term is contributed directly by the applied a.c. field and ψ is the redoxokinetic potential developed. The alternating current flowing through the system can be denoted by

$$i = I \cos (\omega t + \phi). \tag{3}$$

(It is to be noted in this connection that there will be no d.c. component in the current as a condenser has been included in series with the cell while applying the alternating potential and an electron tube measuring instrument is used to measure the d.c. developed.)

As a result of this current there will presumably be a harmonic vibration in the concentrations of M^{m+} and $M^{(m-n)+}$ close to the interface, which will spread into the nearby solution. For the concentration C_1, of the reductant we may write,

$$C_1 = C + \delta C_1 \tag{4}$$

and close to the interface,

$$C_1^\circ = C + \delta C_1^\circ, \tag{5}$$

where

$$\delta C_1^\circ = \Delta C_1^\circ \cos (\omega t + \theta), \tag{6}$$

where ΔC_1° is the amplitude of variation of C_1, close to the interface and θ is the phase angle relative to that of the alternating potential at the microelectrode. Concentration near the interface and not the concentration in the adsorption layer is to be taken into account. The amount in the adsorption layer proper is small and the concentration may be extremely high or low; large changes in concentration in this layer can also be expected due to the passage of the current. But the effective concentration in the adsorption layer is defined by the concentration in the bulk, *i.e.*, near the interface. ΔC_1° represents the fluctuation in this region. A general expression for $\delta C_{1x,t}$ can be obtained by applying Fick's Law of diffusion:

$$\frac{\partial C_1}{\partial t} = D_1 \cdot \frac{\partial^2 C_1}{\partial x^2}, \tag{7}$$

where x is the distance from the electrode surface (regarded as planar) and D_1, is the diffusion coefficient of the reductant.

For the boundary condition given by equation (6) at $x=0$ this gives

$$\partial C_{1x,t} = \Delta C_1^\circ e^{-\sqrt{\omega/2D_1}\cdot x} \cos(\omega t - \sqrt{\omega/2D_1}\cdot x + \phi). \quad (8)$$

This equation represents a diffusion wave of length $2\pi\sqrt{2D_1/\omega}$ and whose amplitude declines exponentially with distance from the interface (compare the solution of corresponding problem in thermal conduction (Carslaw, *Conduction of Heat in Solids*, 1921, p. 47). Applying Faraday's law the current flowing (taking a positive value of i corresponding to the reduction reaction) is given by

$$i = -nFAD_1 \left(\frac{\partial(\delta C_1)}{\partial x}\right)_{x=0} \quad (9)$$

where F is the Faraday and A is the area of the electrode.

Combining equations (8) and (9), we get

$$i = nFA\,\Delta C_1^\circ \sqrt{\omega D_1} \cos\left(\omega t + \theta + \frac{\pi}{4}\right). \quad (10)$$

Comparing equation (10) and (3) we get

$$I = nFA\,\Delta C_1^\circ \sqrt{\omega D_1};\ \phi = \theta + \frac{\pi}{4}. \quad (11)$$

Comparison of equation (10) with the corresponding expression based on the diffusion of the oxidant shows that

$$\frac{\Delta C_1^\circ}{\Delta C_2^\circ} = \sqrt{\frac{D_2}{D_1}},$$

where subscript 2 indicates quantities appertaining to the oxidant. Since D_2 is generally approximately equal to D_1 we shall assume that

$$\Delta C_2^\circ = -\Delta C_1^\circ \quad (12)$$

the minus sign indicating that they are 180° out of phase. Having assumed that $D_1 \simeq D_2$, the subscript on D will be dropped.

Let us now apply the theory of Absolute reaction rates[4] for computing the current. When the micro-electrode is subject to the action of a potential v, a fraction of this potential favours the reduction process and the fraction $(1-\alpha)$ hinders the oxidation process. The sign of v is taken as positive when it is cathodic. The cathodic current i_c is, therefore, given by the equation

$$i_c = nFA\,k_2 C_2^\circ e^{\alpha v nF/RT}, \quad (13)$$

where A is the area of the electrode, k_2 is the rate constant (cm.^{3}/sec.) for the reduction reaction. Similarly the anodic current i_a is given by

$$i_a = nFA\,k_1 C_1^\circ e^{-(1-\alpha)vnF/RT}, \quad (14)$$

where k_1 is the rate constant for the anodic reaction.

Hence the net cathodic current comes out to be

$$i = nFA\left[k_2 C_2^{\circ} e^{\alpha v nF/RT} - k_1 C_1^{\circ} e^{-(1-\alpha) v nF/RT}\right]. \tag{15}$$

Since at $v = 0$ the $i = 0$ and also

$C_1^{\circ} = C_2^{\circ}$, we can write

$$k_1 = k_2 = k \text{ (say)} \tag{16}$$

Further, since in general $C_1^{\circ} = C + \delta C_1^{\circ}$ and $C_2^{\circ} = C - \delta C_1^{\circ}$, we get,

$$i = nFA\,k\left[(C - \delta C_1^{\circ})\, e^{\alpha v nF/RT} - (C + \delta C_1^{\circ})\, e^{-(1-\alpha) v nF/RT}\right] \tag{17}$$

For small values of v, taking the first approximation for the exponential term we get

$$i = nFAkC\left[\frac{vnF}{RT} - \frac{2\delta C_1^{\circ}}{C} - (2\alpha - 1)\cdot\frac{\delta C_1^{\circ}}{C}\cdot\frac{vnF}{RT}\right]. \tag{18}$$

Since the net current passing through the system (when subjected to the alternating field) is zero, we get

$$\int_{t=0}^{t=2\pi/\omega} i\,dt = 0 \tag{19}$$

Combining equations (2), (16), (18) and (19),

we get,

$$\int_{t=0}^{t=2\pi/\omega} nFAkC\left[\frac{VnF}{RT}\cos\omega t + \frac{\psi nF}{RT} - \frac{2\Delta C_1^{\circ}}{C}\cos(\omega t + \theta)\right.$$

$$\left. - \frac{VnF}{RT}\cos(\omega t + \theta) - \frac{\Delta C_1^{\circ}}{C}(2\alpha - 1)\cdot\frac{\psi nF}{RT}\cos(\omega t + \theta)\right] dt = 0. \tag{20}$$

Integrating, we get,

$$\psi = -\frac{2\alpha - 1}{2}\cdot V\cdot\frac{\Delta C_1^{\circ}}{C}\cos\theta. \tag{21}$$

Equation (21) contains the term $\frac{\Delta C_1^{\circ}}{C}\cos\theta$ which can be evaluated as follows:

Differentiating equation (18) we get,

$$\frac{di}{dt} = 2nFAkC\left[\frac{nF}{2RT}\cdot\frac{dv}{dt} - \frac{1}{c}\frac{d(\delta C_1^{\circ})}{dt} - \frac{2\alpha - 1}{2}\cdot\frac{nF}{CRT}\cdot\frac{d(v\delta C_1^{\circ})}{dt}\right]$$

Since $\alpha \cong 0{\cdot}5$ (as seen experimentally later), we get,

$$\frac{di}{dt} = 2nFAkC\left[\frac{nF}{2RT}\cdot\frac{dv}{dt} - \frac{1}{C}\cdot\frac{d(\delta C_1^{\circ})}{dt}\right] \tag{22}$$

Combining (22), (2) and (6), we get,

$$\frac{di}{dt} = 2n\mathrm{F}Ak\mathrm{C}\left[\frac{n\mathrm{F}}{2\mathrm{RT}}\,\omega\,\mathrm{V}\sin\omega t + \frac{\Delta\mathrm{C}_1^{\circ}}{\mathrm{C}}\,\omega\sin(\omega t+\theta)\right] \tag{23}$$

Similarly, differentiating equation (10), we get,

$$\frac{di}{dt} = n\mathrm{F}A\Delta\mathrm{C}_1^{\circ}\sqrt{\frac{\omega\mathrm{D}}{2}}\left[\omega\sin(\omega t+\theta) + \omega\cos(\omega t+\theta)\right] \tag{24}$$

Expanding equations (23) and (24) and equating coefficients of cos ωt gives,

$$-\cot\theta = 1 + 2k\sqrt{\frac{2}{\omega\mathrm{D}}} \tag{25}$$

Similarly, equating coefficients of sin ωt, and combining the result with equation (25), we get,

$$\Delta\mathrm{C}_4^{\circ} = -\frac{k\mathrm{C}n\mathrm{F}\mathrm{V}}{\mathrm{RT}}\sqrt{\frac{2}{\omega\mathrm{D}}}\sin\theta \tag{26}$$

Combining (21), (25) and (26), we get,

$$\psi = (\alpha - \cdot 5)\cdot\frac{\mathrm{V}^2n\mathrm{F}}{2\mathrm{RT}}\,\frac{2+\dfrac{1}{k}\sqrt{\dfrac{\omega\mathrm{D}}{2}}}{2+\dfrac{1}{k^2}\,\dfrac{\omega\mathrm{D}}{2}+\dfrac{2}{k}\sqrt{\dfrac{\omega\mathrm{D}}{2}}} \tag{27}$$

Let us consider two limiting cases:

$$\text{If } \frac{1}{k}\sqrt{\frac{\omega\mathrm{D}}{2}} \ll 2,\quad \psi = \frac{\mathrm{V}^2n\mathrm{F}}{2\mathrm{RT}}(\alpha - \cdot 5) \tag{28}$$

$$\text{If } \frac{1}{k}\sqrt{\frac{\omega\mathrm{D}}{2}} \gg 2,\quad \psi = \frac{\mathrm{V}^2n\mathrm{F}}{2\mathrm{RT}}(\alpha - \cdot 5)\cdot k\cdot\sqrt{\frac{2}{\omega\mathrm{D}}} \tag{29}$$

The following general conclusions can be drawn from the above:—

(*a*) $\psi \propto \mathrm{V}^2$ when ω is constant.

(*b*) At sufficiently low frequencies, ψ is independent of frequency.

(*c*) At higher frequencies, ψ varies inversely proportional to the square-root of frequency.

(*d*) At very high frequencies ψ becomes zero.

The most striking aspect of these results is that under conditions corresponding equation (28) α can be measured, by measuring ψ at known values of V.

3. Experimental

In order to test the theory, it is necessary to measure the redoxokinetic potential at low a.c. fields (not greater than c.a. 15 mv. (r.m.s.). All the

data so far obtained were at much higher a.c. fields. So experiments were specially conducted at low a.c. fields. One of the important features of our apparatus was that the potential measuring device did not draw any appreciable current from the system. This was achieved by combining the pH meter and sensitive galvanometer (L & N) No. 2420. For our present purpose, it was necessary to increase the sensitiveness a hundred-fold or more by using the highly sensitive galvanometer (L & N No. 2239 B). But it was found that the pH meter did not maintain the stability to the necessary degree. So, the pH meter was discarded and the highly sensitive galvanometer was used directly as the null instrument.

The circuit diagram used is given in Fig. 1. The alternating current is supplied by a transformer AB and the current is controlled by the variable resistance R_1. The electrolytic cell contains three electrodes E_1, E_2 and R. E_1 and E_2 conduct the alternating current through the cell. R is the

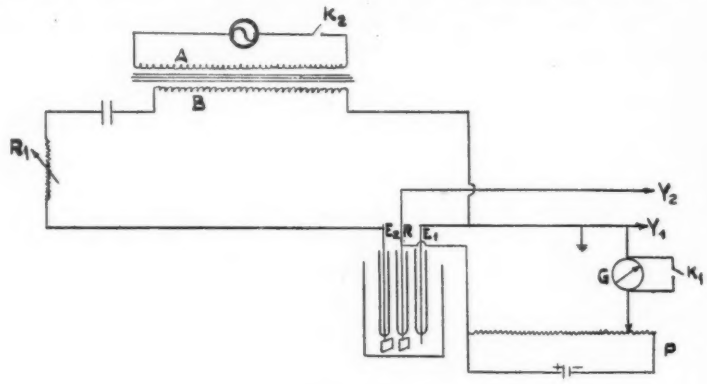

FIG. 1

reference electrode, with reference to which the redoxokinetic potential developed at E_1, (the microelectrode) is measured. At E_2 the potential developed is small as it is a large electrode, and is not normally measured. The a.c. potential existing between E and R is measured by means of the oscillograph. The d.c. potential developed (redoxokinetic potential ψ) between E_1 and R is measured by the potentiometer P, making use of Leeds and Northrope galvanometer [sensitivity: 1 millimeter $= 0{\cdot}416\,\mu v$ (at a distance of 4 metres) and resistance $= 1182$ ohms] as a null instrument. The cell contained ferrous-ferric mixture each at a concentration of 0·005 M. The supporting electrolyte used was 1·0 M sulphuric acid. The solution in the cell was covered with liquid paraffin so as to protect the layer from atmo-

spheric oxidation. The above system was left for twenty-four hours so as to allow it to acquire equilibrium. The key K_2 in the primary of the transformer was used for making a.c. on and off.

Some experiments were also tried by merely taking ferric-ferrous mixture each having concentration M/4 as the electrolyte. To avoid *i*R drop, the reference electrode consisted of a helical spiral placed round the fine electrode E_1. The results obtained are given in Figs. 2 and 3, in which ψ has been plotted against V^2.

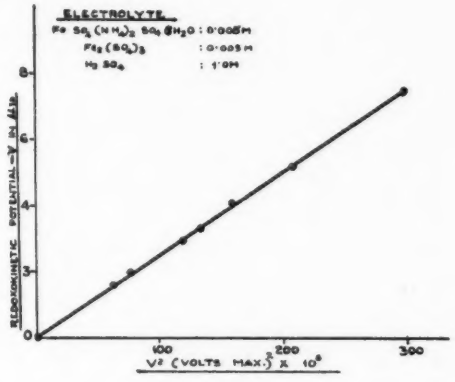

FIG. 2

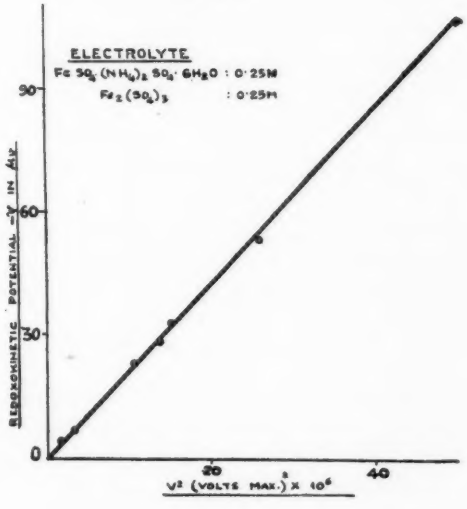

FIG. 3

4. Discussion

An examination of Fig. 2 shows that the magnitude of the redoxokinetic potential is proportional to the square of the a.c. field at the electrode. This is in agreement with the prediction contained in the theoretical equation (27). Further experiments were done with a view to find out the effect of frequency on the system. In these experiments the transformer was replaced by a B.S.R. oscillation type L. 50. No detailed results are indicated here as the change in frequency from 12·5 cycles to 10,000 cycles per sec. did not produce any appreciable change in the redoxokinetic potential. Even this negative result however, is of interest in that it indicates that we are dealing with a system which satisfies equation (28). Applying this equation we get

$$\alpha = 0{\cdot}5 + \frac{2\psi RT}{V^2 nF}.$$

$$\text{If } n = 1 \text{ and } T = 303^\circ \text{ K}, \quad \alpha = 0{\cdot}5 - \frac{0{\cdot}052\,\psi}{V^2}.$$

The value of α comes out to be $0{\cdot}4987 \pm 0{\cdot}0001$.

It is of interest to note that the proportionality between ψ and V^2 also holds for the other system investigated, containing no supporting electrolyte, but having higher concentrations (0·25 molar each) of ferrous and ferric salts. Assuming the formulation to be applicable to this case also, the value of α comes out to be as low as 0·39. The exact significance of this result is a matter for further investigation.

It is to be noted that we have based our formulations on concentrations and not activities and in this regard the α contains in it a function relating to the activity co efficients, though it is expected that the magnitude of the function will be nearly unity due to mutual cancellation of the different terms.

The values of "α" given in this paper are only tentative and illustrative of procedure as the effect of resistance of the system on the value is under investigation, as well as that of the previous history of the platinum electrode.

5. Conclusion

The discovery of the redoxokinetic effect and its theoretical formulation has thus led to a general method for the quantitative determination of the value of α for the first time after the working out of the theory of absolute reaction rates by Glasstone, Laidler, Eyring and others. Though we have described here a system dealing with redox potentials, it can equally well

be applicable to metal solution junction by employing electrodes of the type used by Randles.[3] It is indeed likely that the new effect may throw further light on other aspects of electrode kinetics.

6. Acknowledgement

Our thanks are due to Prof. J. M. Saha, M.Sc., Director, Indian Institute of Sugar Technology for his kind interest, Prof. K. P. Bhatnagar, M.A., LL.B., Principal, D.A.V. College, Kanpur, for kind permission to one of us (H.P.A.) to undertake the investigation at the Indian Institute of Sugar Technology and to the U.P. Scientific Research Committee for a grant which made this work possible.

7. Summary

The theory of the redoxokinetic effect has been formulated for smale a.c. fields. One interesting result coming out of the theory is that the redoxokinetic potential is proportional to the square of the a.c. field. Experiments have been done with the ferrous-ferric system which confirm the above theoretical result. From the observed values of the redoxokinetic potential it has been possible for the first time to get a general method for the d-l termination of "α" a factor introduced in the theory of Absolute reaction rates as applied to electrode processes. The magnitude of this quantity comes out to be $0{\cdot}4987 \pm 0{\cdot}0001$ for ferrous-ferric system (both $0{\cdot}005$ M) containing $1{\cdot}0$ M sulphuric acid as the supporting electrolyte. The corresponding value for the ferrous-ferric system (each $0{\cdot}25$ M) without any supporting electrolyte has been found to be $0{\cdot}39$, which is comparatively low. The exact significance of the latter result needs further investigation. The values of "α" given herein are tentative and illustrative of procedure.

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CHEMISTRY OF GOSSYPOL

Part V. Products of Acetylation of Gossypol

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The earlier methods of Carruth[1] and of Clark[2] for the acetylation of gossypol were improved by Adams, *et al.*,[3] who adopted milder conditions. Still they obtained a mixture of two products which was separated by using difference in solubility. One was a colourless substance melting at 279° and was considered to be the normal acetylation product and hence called gossypol hexa-acetate. The second was a yellow substance melting at 186°. In resembled closely the colourless hexa-acetate in all its reactions but it contained more carbon. Its exact nature was not clearly understood and it was called hexa-acetyl gossypol. This was considered to be a later product obtained from the white hexa-acetate by further change. In their more recent paper Boatner, *et al.*[4] consider that the white substance agrees more closely with the requirements of a tetra-acetate and they were not able to obtain evidence that it undergoes change into the yellow acetyl derivative. In a number of our experiments using Adams' method it appeared that the yellow acetyl derivative is more readily formed directly from gossypol than from gossypol hexa-acetate.

In order to be sure of the purity of the products besides other considerations, attempts have now been made to discover methods yielding a single compound. In this we have been successful. The action of acetyl chloride on gossypol in the presence of pyridine and in the cold is free from complications. It gives a good yield of white gossypol acetate as the sole product and it is readily purified.

The complications that were met with in high temperature acetylation of gossypol would appear to be due to the presence of *ortho*-hydroxy aldehyde groups in gossypol capable of undergoing Perkin's reaction. In an earlier paper of this series[5] the presence of two such groups was established by condensation with acetoacetic ester and malonic ester yielding the α-pyrone derivatives and with acetophenone forming pyrylium salts. By carefully separating the mixture of products obtained by boiling gossypol, sodium acetate and acetic anhydride besides the above mentioned white and yellow

acetyl gossypols a third compound which is more sparingly soluble in solvents and which has a higher melting point could be isolated. This is produced in higher yields on carrying out the heating at 180° for 8 hours. It does not melt below 330° and has the properties of α-pyrone derivatives discussed in the earlier paper.[5]

Experimental

Acetylation of gossypol using acetic anhydride and pyridine.—The following procedure is found to be more convenient for getting the white and yellow gossypol acetates.

Gossypol (1 g.) was treated with acetic anhydride (5 c.c.) and pyridine (0·5 c.c.) and the solution gently refluxed for 30 minutes. The reagents were removed under reduced pressure as completely as possible and the highly viscous residue treated with ether (15 c.c.). On allowing to stand for two hours a white crystalline solid separated out which was filtered, washed with a little ether and recrystallised from a mixture of benzene and ligroin. It formed colourless lens-shaped plates melting at 278–79°. Yield, 0·3 g. It was sparingly soluble in ether but readily in chloroform. In concentrated sulphuric acid it dissolved giving a scarlet red colour to the solution.

The ethereal filtrate which contained the second acetate was evaporated completely and treated with water. The pale yellow solid was filtered, washed, with water and purified by crystallising twice from ligroin. It was obtained as a pale yellow crystalline solid melting at 180–85° with decomposition. It was readily soluble in the common organic solvents and gave a scarlet red colour with concentrated sulphuric acid.

Acetylation of gossypol with acetyl chloride.—Pure gossypol (1 g.) was dissolved in pure anhydrous pyridine (10 c.c.) and the solution cooled in ice. Acetyl chloride (2 c.c.) was then added drop by drop with vigorous stirring during the course of 30 minutes. A white solid separated out during the addition of the reagent. The reaction mixture was allowed to stand for 24 hours and poured into ice-cold water. The solid product was filtered, washed well with water and dried. It was treated with ether and kept for 2 hours whereby the white acetate was obtained almost pure. It was filtered, washed with ether and crystallised from a mixture of benzene and ligroin. It formed colourless lens-shaped plates melting at 278–79°, identical with the white acetate described before. Yield, 0·7–0·9 g. [Found: C, 65·4; H, 5·6; $C_{30}H_{24}O_2$ $(OCOCH_3)_6$ requires C, 65·5 and H, 5·5%.] It is necessary to have quite pure pyridine for the success of the reaction. When this is not assured results are very different.

Perkin's reaction on gossypol.—Gossypol (1 g.) was heated with acetic anyhdride (10 c.c.) and fused sodium acetate (5 g.) at 180° for 8 hours. The ccoled reaction mixture was poured into water and the pale brown solid filtered and washed with water. It was purified by crystallisation from pyridine or ethyl acetate. It was very sparingly soluble in methyl alcohol and other common organic solvents and did not melt below 330°. [Found: C, 68·5; H, 5·3: $C_{34}H_{26}O_4$ $(OCOCH_3)_4$—(α-pyrone derivative) requires C, 68·7; H, 5·2%.]

When the heating was done only for 2 hours and the crude product boiled with methyl alcohol, a small quantity of a solid not melting below 330° was left undissolved. On allowing the alcoholic solution to stand overnight the white acetate separated and from the mother liquor the yellow acetyl derivative could be obtained.

Summary

The white acetate of gossypol is conveniently prepared by employing acetyl chloride and pyridine in the cold for the acetylation. The use of acetic anhydride and a catalyst at elevated temperatures produces a high melting pyrone derivative.

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THE DISPERSION AND THERMO-OPTIC BEHAVIOUR OF VITREOUS SILICA

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(Communicated by Sir C. V. Raman, N.L.)

1. Introduction

As is well known, vitreous silica is obtained by the fusion of crystalline quartz at a temperature abve 1700° C. and subsequent solidification. The chemical composition is unaltered by the process, but there is a considerable diminution in the density which falls from 2·651 to 2·203. Another noteworthy change is the diminution of the coefficient of thermal expansion at room temperatures which is 36×10^{-6} for quartz and only $1{\cdot}5 \times 10^{-6}$ for vitreous silica.

The Raman spectrum of vitreous silica has been studied by several investigators (Gross and Romanova, 1929; Kujumzelis, 1935). It differs from that of crystalline quartz but nevertheless exhibits certain features in common with it. The change may be described by the statement that the sharp lines in the Raman spectrum of quartz become diffuse bands for the vitreous silica.

The infra-red absorption of vitreous silica has been examined upto 8μ (Drummond, 1936). It follows closely the behaviour of quartz, except that the peaks of absorption are not so sharp and well defined.

Tousey (1940) has observed with crystalline quartz two sharp reflection maxima in the ultra-violet analogous to the Reststrahlen in the infra-red, at 1060 A.U. and 1190 A.U. respectively. For vitreous silica he observed two similar bands in almost the same positions to within 20 A.U. but less intense.

In this paper, it is proposed to consider the refractivity, dispersion and the thermo-optic behaviour of vitreous silica, taking into consideration the facts stated aboye.

2. The Refraction and Dispersion of Vitreous Silica

In view of the fact that quartz and vitreous silica are of the same chemical composition and since their spectroscopic behaviour is also closely similar, one expects that it should be possible to calculate the refractivity and

dispersion of vitreous silica from those of quartz by taking into account the disappearance of the optical anisotropy and the diminution of density occurring in its formation. One or another of three well-known formulæ connecting refractive index with density can be used to calculate the refractive index of vitreous silica, namely the Lorentz-Lorenz, the Drude and the Gladstone Dale respectively. In doing this, the index of quartz for each wavelength is obtained by adding twice the ordinary index to the extraordinary index and dividing by three. The observed indices of vitreous silica are given for comparison with the values thus calculated in Table I.

TABLE I

λ (in μ)	Mean n at 18° C. for quartz	n (expt.) at 18° C. for vitreous silica	Lorentz-Lorenz		Drude		Gladstone and Dale	
			n (calc.)	$n_{calc.} - n_{expt.}$	n (calc.)	$n_{calc.} - n_{expt.}$	n (calc.)	$n_{calc.} - n_{expt.}$
·193583	1·664470	1·55999	1·52900	−0·0310	1·57203	+0·0120	1·55218	−0·0078
·20255	1·649850	1·54727	1·51805	−0·0292	1·55910	+0·0118	1·54030	−0·0070
·250329	1·604010	1·50745	1·48344	−0·0240	1·51890	+0·0115	1·50193	−0·0055
·340365	1·570775	1·47867	1·45818	−0·0205	1·48928	+0·0106	1·47432	−0·0044
·434047	1·557110	1·46690	1·44772	−0·0192	1·47778	+0·0109	1·46296	−0·0039
·546072	1·549233	1·46013	1·44168	−0·0185	1·47089	+0·0108	1·45642	−0·0037
·656278	1·544909	1·45640	1·43837	−0·0180	1·46711	+0·0107	1·45282	−0·0036
·794763	1·541449	1·45340	1·43571	−0·0179	1·46408	+0·0107	1·44995	−0·0035
Δn	0·123021	0·10659	0·09329		0·10795		0·10223	

From the table we observe that the error in refractivity is greatest with the Lorentz-Lorenz formula, while the Gladstone and Dale formula gives the best numerical fit. This error varies appreciably with the wavelength for the two formulæ mentioned above, while with the Drude formula it is almost independent of wavelength. At the foot of the table, the change in index as we proceed from the greatest to the least wavelength, Δn, is given. It is seen that the Drude formula represents the dispersion of vitreous silica best. The Gladstone and Dale formula gives good values for the refractivity but not the dispersion, while the Lorentz-Lorenz formula represents neither well. It is, therefore, proposed to consider only the Drude type of formula in the present discussion.

Dispersion formulæ for crystalline quartz have been suggested by many authors in the past. We shall here consider only that put forward by T. Radhakrishnan (1951) in these *Proceedings* which has the following merits: firstly, it fits very well both the ordinary and extraordinary indices over a wide range of wave-lengths, and secondly, all the absorption wave-lengths used in the formula have an experimental justification, except the extreme

ultraviolet wave-length of $0{\cdot}06\,\mu$ which is a hypothetical one. The formulæ respectively for the ordinary and extraordinary indices are:—

$$n_\omega^2 - 1 = \frac{0{\cdot}663044\,\lambda^2}{\lambda^2 - (0{\cdot}0600)^2} + \frac{0{\cdot}517852\,\lambda^2}{\lambda^2 - (0{\cdot}1060)^2} + \frac{0{\cdot}175912\,\lambda^2}{\lambda^2 - (0{\cdot}1190)^2} + \frac{0{\cdot}565380\,\lambda^2}{\lambda^2 - (8{\cdot}844)^2} + \frac{1{\cdot}675299\,\lambda^2}{\lambda^2 - (20{\cdot}742)^2} \quad (1)$$

$$n_\epsilon^2 - 1 = \frac{0{\cdot}665721\,\lambda^2}{\lambda^2 - (0{\cdot}0600)^2} + \frac{0{\cdot}503511\,\lambda^2}{\lambda^2 - (0{\cdot}1060)^2} + \frac{0{\cdot}214792\,\lambda^2}{\lambda^2 - (0{\cdot}1190)^2} + \frac{0{\cdot}539173\,\lambda^2}{\lambda^2 - (8{\cdot}792)^2} + \frac{1{\cdot}8076613\,\lambda^2}{\lambda^2 - (19{\cdot}70)^2} \quad (2)$$

From what has already been pointed out, it is reasonable to expect a similar formula to hold good for vitreous silica. Since the last two terms in the formula are of very minor importance in the visible region of the spectrum, we may without sensible error take the infra-red frequencies for vitreous silica to be those which function in the ordinary index of quartz. When a weighted mean of the oscillator strengths of the corresponding terms for the ordinary and extraordinary indices is taken and reduced proportionately to the density, the constants in the numerators turn out to be 0·5517, 0·4263, 0·1570, 0·46 and 1·43 respectively. From Table I we know that such a calculation would not exactly fit the refractivity of vitreous silica. It is necessary, in fact, to alter the oscillator strengths very slightly. The dispersion of vitreous silica at 18° C. is found to be well represented by the formula.

$$n^2 - 1 = \frac{0{\cdot}5320\,\lambda^2}{\lambda^2 - (0{\cdot}0600)^2} + \frac{0{\cdot}4151\,\lambda^2}{\lambda^2 - (0{\cdot}1060)^2} + \frac{0{\cdot}1570\,\lambda^2}{\lambda^2 - (0{\cdot}1190)^2} + \frac{0{\cdot}4538\,\lambda^2}{\lambda^2 - (8{\cdot}844)^2} + \frac{1{\cdot}4460\,\lambda^2}{\lambda^2 - (20{\cdot}742)^2} \quad (3)$$

The experimental values for the refractive indices (Sosman, 1927) are given with the calculated values in Table II.

TABLE II

λ (in μ)	n (experimental)	n (calculated)
·193583	1·55999	1·55995
·20255	1·54727	1·54732
·231288	1·51941	1·51950
·250329	1·50745	1·50747
·274867	1·49617	1·49624
·396848	1·47061	1·47054
·479991	1·46355	1·46355
·546072	1·46013	1·46012
·643847	1·45674	1·45673
·656278	1·45640	1·45642
·706520	1·45517	1·45517
·794763	1·45340	1·45343

As can be seen, the agreement between the calculated and experimental values is very satisfactory, thereby indicating that the behaviour of quartz and of vitreous silica in regard to refraction and dispersion are very similar to each other. No doubt, a slight change of oscillator strength has been found necessary in the formula, but this is not surprising considering the striking change of structure between these two forms of silica as is revealed by X-ray investigations.

3. The Variation of Refractive Index with Temperature

The refractive indices of vitreous silica increase notably with temperature. Indeed, the increase in index for a given wave-length over a range of 1000° C. is approximately of the same order as the change in index for a particular temperature as we proceed from the visible to the ultra-violet region. Also dn/dt itself varies with wavelength, increasing rapidly with increase of frequency. The thermal expansion of vitreous silica being extremely small, it can contribute very little to the change in refractive index, and even so it would reduce and not increase the index. Thus, considering the position in the light of the remarks already made regarding the dispersion formula of vitreous silica, the only explanation that could reasonably be put forward for the increase of the refractive indices with rise of temperature is that there is a fall in the characteristic absorption frequencies of the material in the ultra-violet region of the spectrum. This indeed is the idea put forward by G. N. Ramachandran (1947 *a*) in his theory of the thermo-optic behaviour of solids. According to him, the temperature variation of the refractivity is due to two causes which usually work in opposite directions, *viz.*, a diminution due to the thermal expansion of the solid and an increase due to the downward shift of the characteristic frequencies of the substance in the ultra-violet. The expression for dn/dt is given by

$$\frac{dn}{dt} = -\frac{r(n^2-1)}{2n} + \frac{1}{n}\sum_r \frac{a_r \lambda^4 \lambda_r^2}{(\lambda^2-\lambda_r^2)^2}\chi_r \qquad (4)$$

where γ is the coefficient of cubical expansion and χ_r is defined as $\frac{1}{\lambda_r}\frac{d\lambda}{dt}$ where λ_r is the characteristic absorption wave-length. In the present treatment, we shall neglect the variations of the infra-red frequencies with temperature, as the contribution of those terms is extremely small. We shall also consider the absorption wave-length in the extreme ultra-violet to be unchanged with temperature. This is justified, as the ultra-violet term arises as a result of inner electronic transitions in the atoms of silicon and oxygen which may be taken to be influenced very little by temperature. Even if they are affected by temperature, the ultra-violet term being sensibly a constant, it would not suffer an appreciable change in value. We are, therefore,

left with two terms for which χ is not equal to zero, namely, the terms containing the wave-lengths 1060 A.U. and 1190 A.U. As these are very close to each other, we shall take it that their χ's are the same.

Measurements of dn/dt have been made for vitreous silica at a mean temperature of 60° C. by Martens (1904) for a series of wavelengths from 1850 A.U. to 6000 A.U. A theoretical evaluation of dn/dt over this range of wave-lengths has already been made by G. N. Ramachandran (1947 *b*). But as the dispersion formula used by him was not the same, it appeared worth while to recalculate the figures using equation (4). In doing so, the value of χ has been taken as $2{\cdot}5 \times 10^{-5}$ which is almost the same as that deduced from the data of Rinne (1914) in the temperature range between 18° C. and 130° C. as shown below. The calculated values are represented by a continuous curve in Fig. 1, while the circles show the experimental data of Martens, and the triangles indicate the data of Tilton and Tool

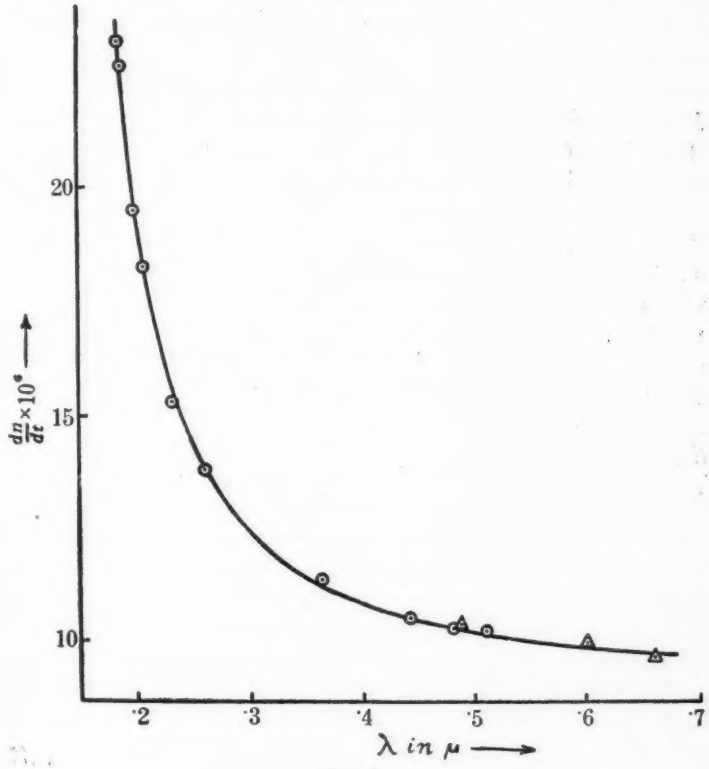

FIG. 1

(1929). It will be seen that the theoretical curve fits the data well over the entire range of wave-lengths.

4. The Shift of the Characteristic Frequencies with Temperature

The refraction of vitreous silica has been studied for a whole range of temperature from $-160°$ C. to $1000°$ C. for four wave-lengths in the visible region by Rinne (1944). The refractive index–temperature curves reveal that the index increases rapidly with temperature from $-160°$ to $475°$ C. Between $475°$ and $590°$ C. the rate of increase shows a drop which is exhibited as a flexure in all the curves about that region. Beyond $590°$ C., the curves again show a rapid rise. The course of the refractive index-temperature curve upto $500°$ C. has been discussed by Ramachandran (1947 *b*). The value of χ used by him in his calculations were obtained by comparison with the χ of the principal Raman line of α quartz, 465 cm.$^{-1}$, as determined by Nedungadi (1940) from $-180°$ to $500°$ C. In this work, it is proposed to actually determine χ at various temperatures from the values of dn/dt from Rinne's data (*loc. cit.*) from $-160°$ to $1000°$ C.

The method of evaluating χ will be described below. From eqn. (4) for dn/dt we notice that on substitution of dn/dt and γ, χ could be calculated. It is, however, important to realise, that, since the dispersion formula fits at $18°$ C., it is possible to evaluate χ from eqn. (4) only at that temperature. The same equation cannot be used to calculate χ at a higher temperature by a mere substitution of the values of dn/dt and γ at the higher temperature. This is because the coefficient of χ in eqn. (4) which is a function of λ_r varies with temperature, or, in other words, the dispersion formula itself is, in reality, different for different temperatures. Therefore, in order to trace the approximate value of χ at various temperatures, the whole range is split up into small intervals. Using the value of χ at $18°$ C., λ_r is deter-

Table III

Range of temperature	$\chi\times10^5$ $\lambda=\cdot47135\,\mu$	$\chi\times10^5$ $\lambda=\cdot501568\mu$	$\chi\times10^5$ $\lambda=\cdot587563\,\mu$	$\chi\times10^5$ $\lambda=\cdot667815\,\mu$	Mean $\chi\times10^5$
$-160°$ to $-64°$ C.	1·3	1·7	1·2	1·0	1·3
$-160°$ to $18°$ C.	1·8	1·6	1·5	1·4	1·6
$-64°$ to $130°$ C.	2·3	2·3	2·3	2·1	2·3
$18°$ to $130°$ C.	2·4	2·8	2·7	2·3	2·6
$18°$ to $235°$ C.	2·8	2·8	2·8	2·6	2·8
$130°$ to $365°$ C.	3·2	3·1	3·1	3·1	3·1
$235°$ to $475°$ C.	3·2	3·5	3·4	3·5	3·4
$365°$ to $590°$ C.	3·1	3·3	3·3	3·4	3·3
$475°$ to $590°$ C.	2·9	2·9	3·0	3·0	3·0
$475°$ to $1000°$ C.	..	3·7	3·6	3·7	3·7
$590°$ to $1000°$ C.	..	3·9	3·8	3·9	3·9

mined at the next higher range. By substituting for dn/dt and γ at this new range, the new value of χ may be calculated. Thus, by successively accounting for λ_r, χ has bean found from $-160°$ to $1000°$ C., and these values are given in Table III.

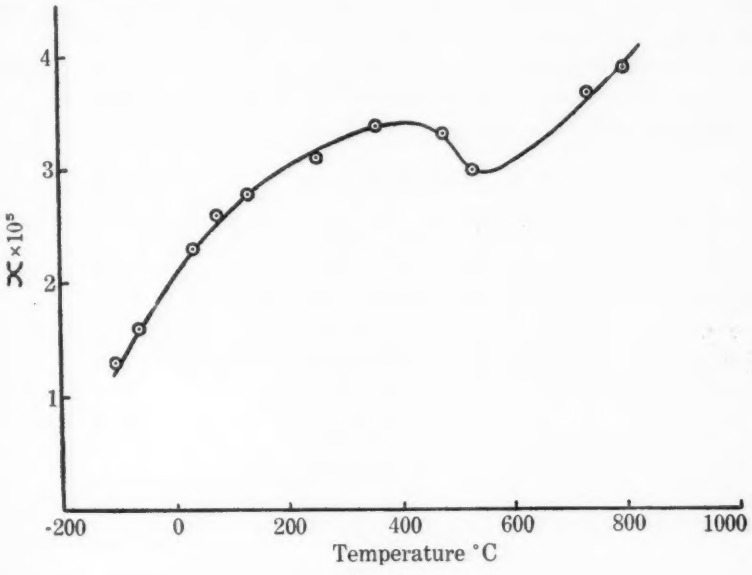

FIG. 2

From Table III we see that there are small differences in the value of χ in each line which are presumably due to the experimental errors in the data. As χ should be independent of the wave-length, its mean value has been given in the last column. A curve drawn connecting χ with temperature is shown in Fig. 2. It is seen that χ first increases with temperature and reaches a maximum at about 400° C., after which it drops, reaching a minimum value at about 560° C. beyond which it again rises rather steeply. The minimum of χ occurs, as nearly as can be judged with the present data, very close to the temperature of transition of quartz from the α to the β form. Various other physical properties of crystalline quartz exhibit noteworthy changes in the temperature range between 400°. and the transition point. It is remarkable that this behaviour characteristic of crystalline quartz manifests itself even in the vitreous modification.

In conclusion, I wish to express my sincere thanks to Prof. Sir C. V. Raman, F.R.S., N.L., for the keen and encouraging interest he took in this investigation.

Summary

The refractivity and the dispersion of vitreous silica are shown to be calculable from those of quartz by considering the diminished density. The temperature variation of its refractive indices over the entire range of wavelengths is in quantitative accord with the hypothesis that the characteristic absorption frequencies in the ultra-violet fall with rise of temperature. The rate of change of these frequencies has been traced from $-160°$ to $1000°$ C. and shows remarkable variations in the vicinity of the temperature at which the α-β transformation in crystalline quartz occurs.

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